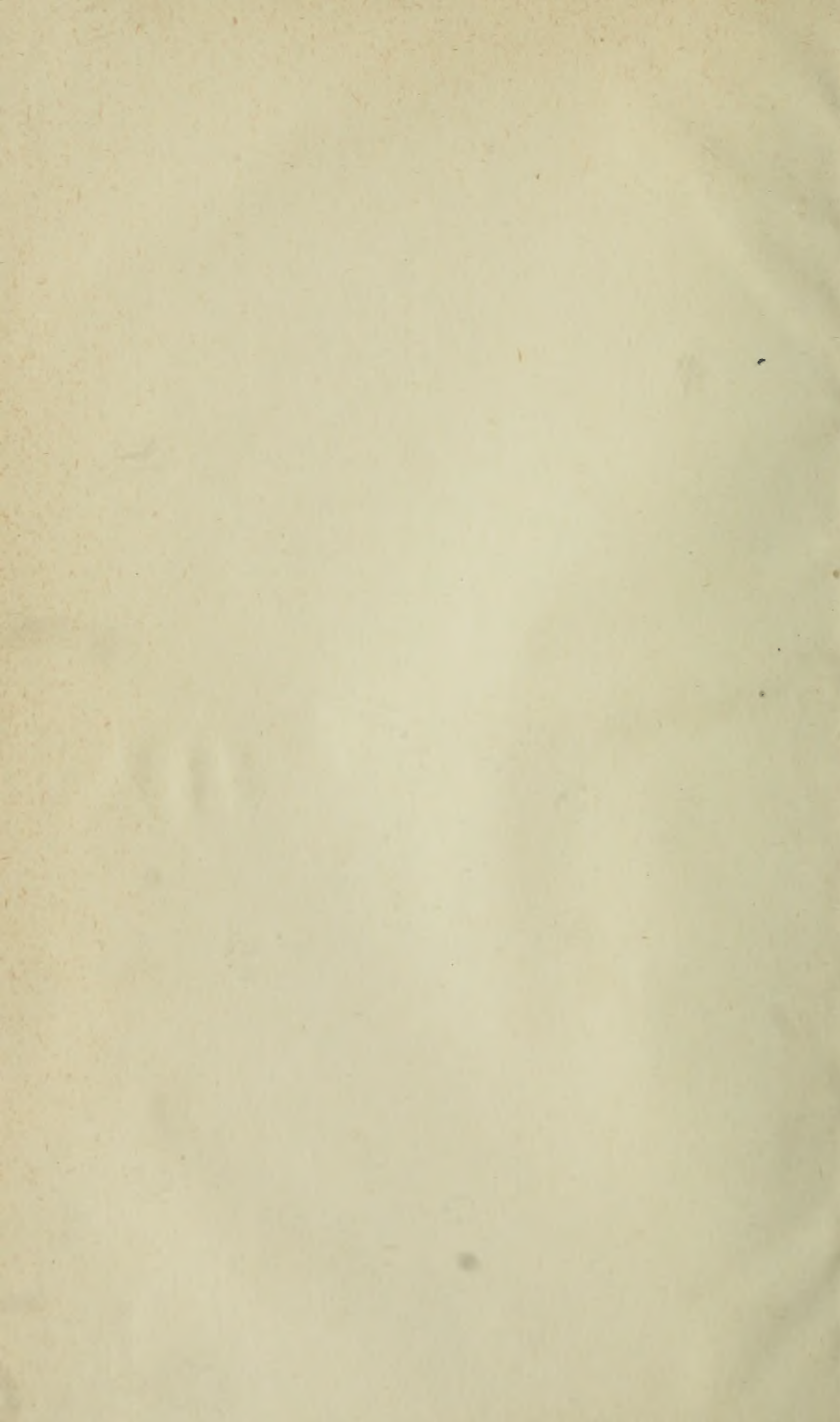


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THE  
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AND  
JOURNAL OF SCIENCE.

CONDUCTED BY

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“Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes.” JUST. LIPS. *Polit. lib. i. cap. 1. Not.*

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VOL. XXXII.—FOURTH SERIES.

JULY—DECEMBER, 1866.

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"Meditationis est perscrutari occulta; contemplationis est admirari  
perspicua . . . . Admiratio generat quæstionem, quæstio investigationem,  
investigatio inventionem."—*Hugo de S. Victore.*

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—"Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condât,  
Quid toties diros cogat flagrare cometas;  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu."

*J. B. Pinelli ad Mazonium.*

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THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
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JOURNAL OF SCIENCE.

[FOURTH SERIES.]

JULY 1866.

I. *On the Determination of the Energy and Entropy of a Body.*  
By Professor R. CLAUSIUS\*.

IN the second Number for this year of the *Zeitschrift für Mathematik und Physik* there is a paper by Bauschinger, chiefly relating to the integral  $\int \frac{dQ}{T}$ , which occurs in the second fundamental theorem of the mechanical theory of heat, where  $dQ$  denotes an element of the quantity of heat which a body takes up in the course of any reversible change of condition, and  $T$  the absolute temperature of the body at the moment of absorbing this element of heat. Bauschinger develops an expression which represents the value of the integral for finite changes of condition under certain simplifying circumstances, and which, for the case where the final condition is the same as the initial condition, and the body accordingly goes through a *circular process*, becomes equal to nothing. In consequence of this last circumstance, Bauschinger supposes that the equation he has developed expresses a general principle, which includes, as a special case, my principle of the equivalence of transformations in circular processes.

I cannot say that I agree with this view of the import of his developments.

In the equation

$$\int \frac{dQ}{T} = 0,$$

which I established for reversible circular processes, there is

\* Translated from the *Zeitschrift für Mathematik und Physik*, vol. xi. part 1, p. 31.

contained a principle applicable to reversible processes in which the initial and final conditions are not identical, a principle which not only have I tacitly regarded as implied therein, but have several times explicitly stated.

If, indeed, the integral  $\int \frac{dQ}{T}$  becomes equal to nought every time that the body, after having passed through various changes, comes back to its initial condition, the expression  $\frac{dQ}{T}$  must be the complete differential of a magnitude which is determined by the existing condition of the body at any given time, without reference to the way in which it came into this condition—that is to say, to the intermediate conditions which it has successively assumed between its initial and its actual conditions. Accordingly, in the case of the condition of the body being determined by any two independent variables, the expression  $\frac{dQ}{T}$  must be the complete differential of a function of these variables; hence, after it has been obtained as a differential expression having reference to these variables, it must satisfy the known conditions of integrability.

The difference between differential expressions which satisfy these conditions, and such as do not satisfy them, is so often mentioned in my papers, that in the collection of my memoirs I have actually made it the subject of a special mathematical introduction. With regard to the expression  $\frac{dQ}{T}$ , it is especially stated that it is a complete differential, and accordingly fulfils the conditions of integrability, and among others that stated in my paper “On a Modified Form of the Second Fundamental Theorem of the Mechanical Theory of Heat”\*.

This being once established, it was self-evident that the integral  $\int \frac{dQ}{T}$  must be susceptible of being expressed as a function of two variables by aid of the proper magnitudes, which in the calculation were supposed to be known. Such a calculation has now been worked out by Bauschinger, the equation which expresses the first fundamental theorem of the mechanical theory of heat being also applied, and special symbols introduced for the differential coefficients  $\frac{dQ}{dv}$  (if the volume  $v$  is assumed to be constant) and  $\frac{dQ}{dT}$  (if the temperature  $T$  is assumed as constant).

\* Poggendorff's *Annalen*, vol. xciii. p. 502; Clausius's *Abhandlungen-sammlung*, part 1, p. 150. [Phil. Mag. S. 4. vol. xii. p. 95.]



Far as I am from denying that such developments may be of great use to the theory of heat, I nevertheless do not think that it can be said of an equation so obtained, that it expresses a new general principle wherein mine is included as a special case. In my opinion, developments of this kind are only to be regarded as the more complete working out of algebraic calculations for which the data were already furnished by the preexisting fundamental equations.

Bauschinger compares his development with those which I have given in my paper "On the Application of the Principle of the Equivalence of Transformations to Internal Work"\*, and contends that I have availed myself of a newly introduced magnitude, which I call Disgregation, and of the hypothesis "that the mechanical work which heat is capable of producing through any change of arrangement is proportional to the absolute temperature at which that change takes place," while he has worked out his development on purely mathematical principles without any such help. He here seems to have overlooked the fact that in this paper I had something quite different in view from what he has treated in his. My object was to determine not only the quantitative value, but much more, the physical signification of

the integral  $\int \frac{dQ}{T}$ ; and as a matter of fact I have established that it may be decomposed into two essentially distinct factors, of which one depends solely on the temperature, and the other solely on the arrangement of the constituents of the body.

When Bauschinger's paper appeared, I had recently completed a new paper which has since been published in the 'Quarterly Journal of the Zurich Society of Natural Science' (*Vierteljahrsschrift d. Züricher naturforschenden Gesellschaft*, vol. x. p. 1), and in Poggendorff's *Annalen* (vol. cxxv. p. 353), in which, among other matters, I have discussed the determination of the integral

$\int \frac{dQ}{T}$ . I have there, as any one may easily convince himself, treated the subject in a more general manner than Bauschinger has done; but nevertheless all the equations which there occur are deduced simply as consequences from the two fundamental equations already named.

It may perhaps be not without interest if I communicate here a few further developments of the same kind, which may serve to complete what are there given, and which appear to me specially fitted to place in a clear light the connexion between this integral and another important magnitude in the theory of heat.

\* Poggendorff's *Annalen*, vol. cxvi. p. 73; *Abhandlungensammlung*, part 1, p. 242. [Phil. Mag. S. 4. vol. xxiv. p. 81.]

But before I proceed to do this, I wish to make a few remarks on a passage in Bauschinger's paper.

At page 114 of the paper, the following equation, likewise relating to the second fundamental theorem of the mechanical theory of heat, is discussed:

$$\frac{dQ}{dv} = A(a+t) \frac{dp}{dt}.$$

Here  $\frac{dQ}{dv}$  is the differential coefficient which has already been once mentioned above,  $p$  denotes the pressure to which the body is exposed,  $t$  the temperature of the body reckoned from the freezing-point, and  $a$  the reciprocal of the coefficient of expansion of gases (that is, approximately the number 273), so that  $a+t$  is the same quantity that has been previously denoted by  $T$ ; lastly,  $A$  denotes the thermal equivalent of the unit of work. This equation is referred to by Bauschinger as "the equation already established in another form by Carnot."

These words might easily lead to a misconception. The equation which occurs in the older expositions of Carnot's theory, but which, strictly speaking, is not due to Carnot, having been first deduced by Clapeyron from Carnot's theorem, when put into a form the most closely resembling the above that it is capable of assuming, runs thus,

$$\frac{dQ}{dv} = C \frac{dp}{dt},$$

where  $C$  denotes an undefined function of the temperature, which has often been called Carnot's function. If now this function, previously left undefined, is replaced in this equation by the definite function  $A(a+t)$ , there is certainly something more than what we are accustomed to understand by a mere change of form.

I now pass on to the developments above announced.

### § 1.

We will in this development again take as our starting-point the two fundamental equations already mentioned, by means of which I have expressed the two fundamental theorems in my paper "On a Modified Form of the Second Fundamental Theorem of the Mechanical Theory of Heat."

The first fundamental equation, when taken as relating to an infinitely small change of condition in any body chosen for consideration, is

$$dQ = dU + AdW. \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Here, as before,  $A$  denotes the thermal equivalent of work (that is to say, the heat-equivalent of the unit of work), and  $dQ$  the

quantity of heat absorbed during an infinitely small change of the body's condition.  $dW$  further expresses the external work simultaneously performed by the body, and  $dU$  the alteration which is thereby produced in the magnitude, denoted in the title of this paper by the word ENERGY. When I introduced the magnitude  $U$  into the theory of heat for the first time\*, I gave it no particular name, but contented myself with defining its signification by a definition which amounted to saying that this magnitude was the sum of the actual heat gained by a body and of that consumed in internal work, starting from any given initial condition. Since, however, W. Thomson, who subsequently introduced this same magnitude into his equations, has proposed for it the convenient name of *Energy*, I have adopted this expression.

The peculiarity of the magnitude  $U$ , whereby it is distinguished from the other variable quantities occurring in the above equation, is this, that the initial condition of the body being supposed given, it is completely defined by the actual condition of the body at any time, without reference to the way in which the body arrived at that condition, whereas the magnitudes  $W$  and  $Q$  depend not only on the actual condition of the body, but also on the manner of its transition to that condition from its initial state.

A slight simplification can still be introduced into the above equation. In one of the Additions to be found in my 'Collection of Memoirs,' I have proposed to speak of mechanical work, when it is expressed not in the usual measure, but in heat-measure (that is, when we adopt for it as unit the quantity of work corresponding to a unit of heat) by the name of WORK†. Accordingly, since  $W$  denotes the external work expressed in mechanical units, the product  $AW$  denotes the external work expressed in thermal units. We will express this by a particular letter, thus,

$$w = AW.$$

The above equation then runs,

$$dQ = dU + dw. \quad . \quad . \quad . \quad . \quad . \quad (I a)$$

## § 2.

The second fundamental equation with which we have to do here is the one already mentioned as applying to reversible cir-

\* Poggendorff's *Annalen*, vol. lxxix. p. 384, March 1850; *Abhandlungen-sammlung*, part 1, p. 32.

† [The German word is "Werk" in contradistinction to "Arbeit." The latter word having been rendered throughout by *work*, in accordance with prevailing English usage, it is not easy to reproduce without circumlocution the distinction intended in the original between *Arbeit* and *Werk*. —TRANSL.]





generally by  $x$  and  $y$ . We can afterwards put in the place of these undefined variables definite magnitudes, such as temperature, volume, pressure, or any others appropriate to the particular investigation in view.

If the condition of the body is defined by the two variables  $x$  and  $y$ , all magnitudes which are defined by the actually existing condition of the body, independently of the way in which the body came into this condition, must be capable of being expressed by functions of these variables, in which the variables themselves may be regarded as independent of each other. Accordingly the magnitudes  $S$  and  $U$  must likewise be regarded as functions of the independent variables  $x$  and  $y$ .

This, however, does not hold good respecting the magnitude  $w$ , since, even if it is agreed that only reversible processes are to occur, the external work (*Werk*), which is performed during the passage of the body from a given initial to a given final condition, depends not only on what the initial and final conditions are, but also upon the succession of intermediate conditions through which it passes, or upon the way in which the change takes place. The differential coefficients  $\frac{dw}{dx}$  and  $\frac{dw}{dy}$  are indeed definite functions of  $x$  and  $y$ ; but if the former is differentiated with respect to  $y$ , and the latter with respect to  $x$ , the resulting differential coefficients of the second order,  $\frac{d}{dy}\left(\frac{dw}{dx}\right)$  and  $\frac{d}{dx}\left(\frac{dw}{dy}\right)$ , are not equal to each other, as must be the case if,  $x$  and  $y$  being variables independent of each other, the magnitude  $w$  could be expressed as a function of them.

If now in equation (I) we put

$$dS = \frac{dS}{dx} dx + \frac{dS}{dy} dy,$$

$$dU = \frac{dU}{dx} dx + \frac{dU}{dy} dy,$$

$$dw = \frac{dw}{dx} dx + \frac{dw}{dy} dy,$$

it is transformed into

$$T \frac{dS}{dx} dx + T \frac{dS}{dy} dy = \left( \frac{dU}{dx} + \frac{dw}{dx} \right) dx + \left( \frac{dU}{dy} + \frac{dw}{dy} \right) dy.$$

Since this equation must be true for any values of the differentials  $dx$  and  $dy$ , and therefore for that case, amongst others, in which one or other of the differentials is made equal to nought,

it splits up at once into the two following equations :

$$\left. \begin{aligned} T \frac{dS}{dx} &= \frac{dU}{dx} + \frac{dw}{dx}, \\ T \frac{dS}{dy} &= \frac{dU}{dy} + \frac{dw}{dy}. \end{aligned} \right\} \cdot \cdot \cdot \cdot (2)$$

From these equations the magnitudes S and U can be eliminated by a second differentiation.

#### § 4.

We will first eliminate the magnitude U, since the equation that so results is the simpler of the two.

For this purpose we differentiate the first of the equations (2) with respect to  $y$ , and the second with respect to  $x$ . In so doing we will write the differential coefficients of S and U of the second order quite in the usual way. The differential coefficients  $\frac{dw}{dx}$  and  $\frac{dw}{dy}$ , on the other hand, we will write as above,  $\frac{d}{dy} \left( \frac{dw}{dx} \right)$  and  $\frac{d}{dx} \left( \frac{dw}{dy} \right)$ , in order to express formally that they are not differential coefficients of the second order of a function of  $x$  and  $y$ . Lastly, we have to consider that the magnitude T which occurs in these equations, namely the absolute temperature of the body, is also to be regarded as a function of  $x$  and  $y$ . We thus obtain

$$\begin{aligned} \frac{dT}{dy} \cdot \frac{dS}{dx} + T \frac{d^2S}{dxdy} &= \frac{d^2U}{dxdy} + \frac{d}{dy} \left( \frac{dw}{dx} \right), \\ \frac{dT}{dx} \cdot \frac{dS}{dy} + T \frac{d^2S}{dydx} &= \frac{d^2U}{dydx} + \frac{d}{dx} \left( \frac{dw}{dy} \right). \end{aligned}$$

Subtracting the second of these equations from the first, and remembering that

$$\frac{d^2S}{dxdy} = \frac{d^2S}{dydx} \quad \text{and} \quad \frac{d^2U}{dxdy} = \frac{d^2U}{dydx},$$

we obtain

$$\frac{dT}{dy} \cdot \frac{dS}{dx} - \frac{dT}{dx} \cdot \frac{dS}{dy} = \frac{d}{dy} \left( \frac{dw}{dx} \right) - \frac{d}{dx} \left( \frac{dw}{dy} \right). \quad \cdot \cdot \cdot (3)$$

The difference which occurs here in the right-hand member plays an important part in the mechanical theory of heat. In my last published paper I have called it *difference of work* (Werk) in relation to  $xy$ , and have denoted it by  $E_{xy}$ ; so that we may put

$$E_{xy} = \frac{d}{dy} \left( \frac{dw}{dx} \right) - \frac{d}{dx} \left( \frac{dw}{dy} \right). \quad \cdot \cdot \cdot (4)$$



The foregoing equation is thus transformed into

$$\frac{dT}{dy} \cdot \frac{dS}{dx} - \frac{dT}{dx} \cdot \frac{dS}{dy} = E_{xy}. \quad (5)$$

This is the differential equation resulting from equation (1) which serves to define S.

In order now to eliminate the magnitude S from the two equations (2), we will write them as follows:—

$$\frac{dS}{dx} = \frac{1}{T} \cdot \frac{dU}{dx} + \frac{1}{T} \cdot \frac{dw}{dx},$$

$$\frac{dS}{dy} = \frac{1}{T} \cdot \frac{dU}{dy} + \frac{1}{T} \cdot \frac{dw}{dy}.$$

Of these equations, again, we will differentiate the first with respect to  $y$ , and the second with respect to  $x$ , whereby we get

$$\frac{d^2S}{dxdy} = \frac{1}{T} \cdot \frac{d^2U}{dxdy} - \frac{1}{T^2} \cdot \frac{dT}{dy} \cdot \frac{dU}{dx} + \frac{d}{dy} \left( \frac{1}{T} \cdot \frac{dw}{dx} \right),$$

$$\frac{d^2S}{dydx} = \frac{1}{T} \cdot \frac{d^2U}{dydx} - \frac{1}{T^2} \cdot \frac{dT}{dx} \cdot \frac{dU}{dy} + \frac{d}{dx} \left( \frac{1}{T} \cdot \frac{dw}{dy} \right).$$

Subtracting the second of these equations from the first, bringing all the terms of the resulting equation in which U occurs to the left-hand side, and multiplying the whole equation by  $T^2$ , we have

$$\frac{dT}{dy} \cdot \frac{dU}{dx} - \frac{dT}{dx} \cdot \frac{dU}{dy} = T^2 \left[ \frac{d}{dy} \left( \frac{1}{T} \cdot \frac{dw}{dx} \right) - \frac{d}{dx} \left( \frac{1}{T} \cdot \frac{dw}{dy} \right) \right]. \quad (6)$$

For the magnitude which here stands on the right-hand side we will likewise employ a special symbol, putting

$$E'_{xy} = T^2 \left[ \frac{d}{dy} \left( \frac{1}{T} \cdot \frac{dw}{dx} \right) - \frac{d}{dx} \left( \frac{1}{T} \cdot \frac{dw}{dy} \right) \right]. \quad (7)$$

The last equation then becomes

$$\frac{dT}{dy} \cdot \frac{dU}{dx} - \frac{dT}{dx} \cdot \frac{dU}{dy} = E'_{xy}. \quad (8)$$

This is the differential equation, resulting from equation (1), which serves to define U.

## § 5.

Before pursuing further the treatment of the two differential equations (5) and (8), it will be advisable to direct attention

for a moment to the magnitudes  $E_{xy}$  and  $E'_{xy}$  which therein occur.

Between these two magnitudes the following relation exists, which can be easily deduced from the expressions given in (4) and (7),

$$E'_{xy} = TE_{xy} - \frac{dT}{dy} \cdot \frac{dw}{dx} + \frac{dT}{dx} \cdot \frac{dw}{dy} \quad . \quad . \quad . \quad (9)$$

Both the magnitudes  $E_{xy}$  and  $E'_{xy}$  are functions of  $x$  and  $y$ . If in order to define the body we select, instead of  $x$  and  $y$ , any other two variables, which we may call  $\xi$  and  $\eta$ , and form with them the corresponding magnitudes  $E_{\xi\eta}$  and  $E'_{\xi\eta}$ , namely,

$$E_{\xi\eta} = \frac{d}{d\eta} \left( \frac{dw}{d\xi} \right) - \frac{d}{d\xi} \left( \frac{dw}{d\eta} \right), \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$E'_{\xi\eta} = T^2 \left[ \frac{d}{d\eta} \left( \frac{1}{T} \cdot \frac{dw}{d\xi} \right) - \frac{d}{d\xi} \left( \frac{1}{T} \cdot \frac{dw}{d\eta} \right) \right], \quad . \quad (11)$$

these magnitudes are of course functions of  $\xi$  and  $\eta$ , just as the foregoing magnitudes are functions of  $x$  and  $y$ . But if now one of the last two expressions, *e. g.* the one for  $E_{\xi\eta}$ , is compared with the expression for the corresponding magnitude  $E_{xy}$ , we find that they represent, not merely expressions for the same magnitude with reference to different variables, but actually different magnitudes. For this reason I have not called  $E_{xy}$  simply the difference of work, but the difference of work in relation to  $xy$ , whereby it is at once distinguished from  $E_{\xi\eta}$ , or the difference of work in relation to  $\xi$  and  $\eta$ . The same holds good of  $E'_{xy}$  and  $E'_{\xi\eta}$ , which are also to be regarded as two different magnitudes.

The relation existing between the magnitudes  $E_{xy}$  and  $E_{\xi\eta}$  may be found as follows. The differential coefficients occurring in the expression given for  $E_{\xi\eta}$  in (10) may be arrived at by first forming the differential coefficients in relation to the variables  $x$  and  $y$ , and then treating each of these two variables as a function of  $\xi$  and  $\eta$ . In this way we obtain

$$\begin{aligned} \frac{dw}{d\xi} &= \frac{dw}{dx} \cdot \frac{dx}{d\xi} + \frac{dw}{dy} \cdot \frac{dy}{d\xi}, \\ \frac{dw}{d\eta} &= \frac{dw}{dx} \cdot \frac{dx}{d\eta} + \frac{dw}{dy} \cdot \frac{dy}{d\eta}. \end{aligned}$$

Let the first of these two expressions be differentiated with respect to  $\eta$  and the second with respect to  $\xi$ , and we then get, by the application of the same process,

$$\frac{d}{d\eta} \left( \frac{dw}{d\xi} \right) = \left\{ \begin{array}{l} \frac{d}{dx} \left( \frac{dw}{dx} \right) \cdot \frac{dx}{d\xi} \cdot \frac{dx}{d\eta} + \frac{d}{dy} \left( \frac{dw}{dx} \right) \cdot \frac{dx}{d\xi} \cdot \frac{dy}{d\eta} + \frac{dw}{dx} \cdot \frac{d^2x}{d\xi d\eta} \\ + \frac{d}{dx} \left( \frac{dw}{dy} \right) \cdot \frac{dx}{d\eta} \cdot \frac{dy}{d\xi} + \frac{d}{dy} \left( \frac{dw}{dy} \right) \cdot \frac{dy}{d\xi} \cdot \frac{dy}{d\eta} + \frac{dw}{dy} \cdot \frac{d^2y}{d\xi d\eta} \end{array} \right.$$

$$\frac{d}{d\xi} \left( \frac{dw}{d\eta} \right) = \left\{ \begin{array}{l} \frac{d}{dx} \left( \frac{dw}{dx} \right) \cdot \frac{dx}{d\xi} \cdot \frac{dx}{d\eta} + \frac{d}{dy} \left( \frac{dw}{dx} \right) \cdot \frac{dx}{d\eta} \cdot \frac{dy}{d\xi} + \frac{dw}{dx} \cdot \frac{d^2x}{d\xi d\eta} \\ + \frac{d}{dx} \left( \frac{dw}{dy} \right) \cdot \frac{dx}{d\xi} \cdot \frac{dy}{d\eta} + \frac{d}{dy} \left( \frac{dw}{dy} \right) \cdot \frac{dy}{d\xi} \cdot \frac{dy}{d\eta} + \frac{dw}{dy} \cdot \frac{d^2y}{d\xi d\eta} \end{array} \right.$$

If the second of these equations is subtracted from the first, most of the terms on the right-hand side disappear, and there remain only four terms, which may be thus contracted into a product of two binomial expressions—

$$\frac{d}{d\eta} \left( \frac{dw}{d\xi} \right) - \frac{d}{d\xi} \left( \frac{dw}{d\eta} \right) = \left( \frac{dx}{d\xi} \cdot \frac{dy}{d\eta} - \frac{dx}{d\eta} \cdot \frac{dy}{d\xi} \right) \left[ \frac{d}{dy} \left( \frac{dw}{dx} \right) - \frac{d}{dx} \left( \frac{dw}{dy} \right) \right].$$

The expression standing on the left-hand side of this equation is  $E_{\xi\eta}$ , and that contained within square brackets on the right-hand side is  $E_{xy}$ . Hence we finally obtain

$$E_{\xi\eta} = \left( \frac{dx}{d\xi} \cdot \frac{dy}{d\eta} - \frac{dx}{d\eta} \cdot \frac{dy}{d\xi} \right) E_{xy}. \quad (12)$$

Similarly we may also find

$$E'_{\xi\eta} = \left( \frac{dx}{d\xi} \cdot \frac{dy}{d\eta} - \frac{dx}{d\eta} \cdot \frac{dy}{d\xi} \right) E'_{xy}. \quad (13)$$

If we replace only one of the variables by a new one—if, for instance, we retain the variable  $x$  while putting the variable  $\eta$  in place of  $y$ , we have in the two foregoing equations  $x = \xi$ , and consequently  $\frac{dx}{d\xi} = 1$ , and  $\frac{dx}{d\eta} = 0$ , whereby they become

$$E_{x\eta} = \frac{dy}{d\eta} E_{xy} \text{ and } E'_{x\eta} = \frac{dy}{d\eta} E'_{xy}. \quad (14)$$

If, indeed, the original variables are retained but their order of succession altered, the equations in question take the opposite sign, as may be seen at once from a glance at the expressions (4) and (7); that is to say, they become

$$E_{yx} = -E_{xy} \text{ and } E'_{yx} = -E'_{xy}. \quad (15)$$

## § 6.

We now return again to the differential equations (5) and (8) that have been deduced for  $S$  and  $U$ .

These assume particularly simple forms when the temperature  $T$  is taken as one of the independent variables. If, for instance, we put  $T=y$ , it follows thence that  $\frac{dT}{dy}=1$  and  $\frac{dT}{dx}=0$ ; and we have also, in place of  $E_{xy}$  and  $E'_{xy}$ , to write  $E_{xT}$  and  $E'_{xT}$ . Equations (5) and (8) thus become

$$\frac{dS}{dx} = E_{xT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\frac{dU}{dx} = E'_{xT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

These equations can at once be integrated with respect to  $x$ , and we so get

$$S = \int E_{xT} dx + \phi(T), \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$U = \int E'_{xT} dx + \psi(T), \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where  $\phi(T)$  and  $\psi(T)$  are two arbitrary functions of  $T$ .

The last two equations can of course be easily changed back again by putting any other variable  $y$  in place of the variable  $T$ . For this purpose we only require to substitute for  $T$  the function of  $x$  and  $y$  which represents this magnitude. The equations hence resulting are the same as those obtained when we start from the more general differential equations (5) and (8), and apply to them the common process of integration, keeping in mind, at the same time, that according to (14) we have to put

$$\frac{dy}{dT} E_{xy} = E_{xT} \quad \text{and} \quad \frac{dy}{dT} E'_{xy} = E'_{xT}.$$

We have thus in what precedes arrived, by help of the partial differential equations deduced from equation (1), at expressions for  $S$  and  $U$ , each of which still contains an arbitrary function of  $T$ . If we want to determine these functions, which are there left arbitrary, we must go back to equations (I a) and (II a), whence equation (1) was obtained by elimination of  $dQ$ .

## § 7.

Let us assume that the condition of the body is determined by its temperature and any other variable  $x$ , we can then give to the two equations (I a) and (II a) the following form :

$$\frac{dS}{dT} dT + \frac{dS}{dx} dx = \frac{1}{T} \cdot \frac{dQ}{dT} dT + \frac{1}{T} \cdot \frac{dQ}{dx} dx,$$

$$\frac{dU}{dT} dT + \frac{dU}{dx} dx = \left( \frac{dQ}{dT} - \frac{dw}{dT} \right) dT + \left( \frac{dQ}{dx} - \frac{dw}{dx} \right) dx.$$



Since these equations must be true for any values of the differentials  $dT$  and  $dx$ , each of them splits up, as has been already pointed out in a similar case above, into two equations. Of the four equations so arising we will here employ only those two which can serve for the determination of  $\frac{dS}{dT}$  and of  $\frac{dU}{dT}$ , namely

$$\frac{dS}{dT} = \frac{1}{T} \cdot \frac{dQ}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$\frac{dU}{dT} = \frac{dQ}{dT} - \frac{dw}{dT}. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

In order to determine the two other differential coefficients  $\frac{dS}{dx}$  and  $\frac{dU}{dx}$ , we will apply equations (16) and (17) deduced above. With the aid of these expressions of the four differential coefficients we can form the following complete differential equations of  $S$  and  $U$ :

$$dS = \frac{1}{T} \cdot \frac{dQ}{dT} dT + E_{xT} dx, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$dU = \left( \frac{dQ}{dT} - \frac{dw}{dT} \right) dT + E'_{xT} dx. \quad . \quad . \quad . \quad . \quad (23)$$

Since the magnitudes  $S$  and  $U$  must be capable of being represented by functions of  $T$  and  $x$ , in which the two variables  $T$  and  $x$  may be looked upon as independent of each other, the known equation of condition of integrability must apply to both the foregoing equations. For the first equation this is

$$\frac{d}{dx} \left( \frac{1}{T} \cdot \frac{dQ}{dT} \right) = \frac{dE_{xT}}{dT},$$

or, differently written,

$$\frac{d}{dx} \left( \frac{dQ}{dT} \right) = T \frac{dE_{xT}}{dT}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

For the second equation the equation of condition is

$$\frac{d}{dx} \left( \frac{dQ}{dT} \right) - \frac{d}{dx} \left( \frac{dw}{dT} \right) = \frac{dE'_{xT}}{dT}. \quad . \quad . \quad . \quad . \quad (25)$$

These two equations of condition are connected with each other in such a manner that from either of them the necessity of the other can be immediately deduced. Between the two magnitudes  $E_{xT}$  and  $E'_{xT}$ , which occur in them, the following



the external work (Werk) *expressed in thermal units*

$$dw = A p dv. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Let us now suppose that the condition of the body is determined by the magnitudes  $x$  and  $y$ , then  $v$  must be regarded as a function of  $x$  and  $y$ , and the last equation may be written thus,

$$\frac{dw}{dx} dx + \frac{dw}{dy} dy = A p \left( \frac{dv}{dx} dx + \frac{dv}{dy} dy \right),$$

whence we immediately get the two following equations :

$$\frac{dw}{dx} = A p \frac{dv}{dx},$$

$$\frac{dw}{dy} = A p \frac{dv}{dy}.$$

By introducing these values into the expressions given for  $E_{xy}$  and  $E'_{xy}$  in (4) and (7), we have

$$E_{xy} = A \left[ \frac{d}{dy} \left( p \frac{dv}{dx} \right) - \frac{d}{dx} \left( p \frac{dv}{dy} \right) \right],$$

$$E'_{xy} = A T^2 \left[ \frac{d}{dy} \left( \frac{p}{T} \cdot \frac{dv}{dx} \right) - \frac{d}{dx} \left( \frac{p}{T} \cdot \frac{dv}{dy} \right) \right].$$

In the last of these equations we will put, for shortness,

$$\pi = \frac{p}{T} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

whereby it becomes

$$E'_{xy} = A T^2 \left[ \frac{d}{dy} \left( \pi \frac{dv}{dx} \right) - \frac{d}{dx} \left( \pi \frac{dv}{dy} \right) \right].$$

Performing now the differentiation of the products in these expressions, bearing in mind that  $\frac{d^2 v}{dx dy} = \frac{d^2 v}{dy dx}$ , we obtain

$$E_{xy} = A \left( \frac{dp}{dy} \cdot \frac{dv}{dx} - \frac{dp}{dx} \cdot \frac{dv}{dy} \right), \quad . \quad . \quad . \quad . \quad (30)$$

$$E'_{xy} = A T^2 \left( \frac{d\pi}{dy} \cdot \frac{dv}{dx} - \frac{d\pi}{dx} \cdot \frac{dv}{dy} \right). \quad . \quad . \quad . \quad (31)$$

If it be assumed that one of the independent variables by which the condition of the body is determined (for instance, the variable which we have hitherto denoted by  $y$ ) is the temperature of the body, all that is needful to do is to write everywhere

T instead of  $y$ ; thus,

$$E_T = A \left( \frac{dp}{dT} \cdot \frac{dv}{dx} - \frac{dp}{dx} \cdot \frac{dv}{dT} \right), \quad . \quad . \quad . \quad (32)$$

$$E_{xT} = AT^2 \left( \frac{d\pi}{dT} \cdot \frac{dv}{dx} - \frac{d\pi}{dx} \cdot \frac{dv}{dT} \right). \quad . \quad . \quad . \quad (33)$$

Applying now these expressions to equations (22) and (23), and at the same time putting therein  $\frac{dw}{dT} = Ap \frac{dv}{dT}$ , we have

$$dS = \frac{1}{T} \cdot \frac{dQ}{dT} dT + A \left( \frac{dp}{dT} \cdot \frac{dv}{dx} - \frac{dp}{dx} \cdot \frac{dv}{dT} \right) dx, \quad . \quad . \quad . \quad (34)$$

$$dU = \left( \frac{dQ}{dT} - Ap \frac{dv}{dT} \right) dT + AT^2 \left( \frac{d\pi}{dT} \cdot \frac{dv}{dx} - \frac{d\pi}{dx} \cdot \frac{dv}{dT} \right) dx. \quad (35)$$

These expressions become particularly simple if we take for the second variable  $x$ , hitherto left undetermined, the volume  $v$ , for we then have to make  $\frac{dv}{dx} = 1$ , and  $\frac{dv}{dT} = 0$ . We thus get

$$dS = \frac{1}{T} \cdot \frac{dQ}{dT} dT + A \frac{dp}{dT} dv, \quad . \quad . \quad . \quad (36)$$

$$dU = \frac{dQ}{dT} dT + AT^2 \frac{d\pi}{dT} dv. \quad . \quad . \quad . \quad (37)$$

For the case in which the change of volume in the body takes place without any partial change of its state of aggregation, the differential coefficient  $\frac{dQ}{dT}$  which occurs in the last equations is simply the product of the weight of the body into its specific heat at constant volume. Denoting this specific heat by  $c$ , and the weight of the body by  $M$ , the equations become, for this case,

$$dS = M \frac{c}{T} dT + A \frac{dp}{dT} dv, \quad . \quad . \quad . \quad (38)$$

$$dU = McdT + AT^2 \frac{d\pi}{dT} dv. \quad . \quad . \quad . \quad (39)$$

As will be easily understood, we might specialize the above equations in various other ways, by choosing particular magnitudes as variables, or by applying the equations to particular classes of bodies. I will not, however, enter further either upon this point or upon the performance of the integration of the complete differential equations, inasmuch as I have treated some



cases of this kind by way of illustration in my last-published paper already referred to.

I hope that the above comprehensive survey of the differential equations relating to Entropy and Energy may contribute to make mathematicians and physicists better acquainted with magnitudes which play so important a part in the mechanical theory of heat, and to render the employment of them easier to them. In particular, I consider that the parallel treatment throughout of these two magnitudes presents the advantage of rendering distinctly evident how far they resemble each other, and wherein they differ.

Zürich, July 24, 1865.

## II. Archdeacon PRATT'S *Reply to Captain A. R. CLARKE'S Remarks on his Determination of the Figure of the Earth from Geodetic Data*.\*

I HAVE read the remarks of Captain Clarke, in your Number for March, on my method of determining the mean figure of the earth from geodetic data, as set forth in the third edition of my 'Figure of the Earth,' with the care which anything proceeding from such an authority on such a subject justly demands; but I see nothing in them to convince me that Bessel's method is not erroneous. In the present communication I hope to make this matter clear. I propose, first, to point out in what Bessel's method is erroneous; secondly, to explain my own method, as already published; thirdly, to suggest an improvement of my method.

### I. *To point out in what Bessel's method is erroneous.*

2. In obtaining by geodesy the figure of the earth, there are two classes of errors which we have to diminish as much as possible—those arising from observation and measurement, and those arising from the irregularities of the actual surface and mass of the earth, as far as it differs from being a perfect spheroid of equilibrium. The latter class is, as all now acknowledge, much the most important. Captain Clarke says of these errors, that they "are in their average magnitude very much larger than the probable errors of astronomical determinations of latitude, and indeed overwhelm the errors of the geodetical operations." Bessel's method for diminishing both classes of errors, which he attempts to do by one process, Captain Clarke explains with great perspicuity. Each arc is subdivided into subordinate arcs, and corrections,

$$x, m + \alpha u + \beta v + x, \dots,$$

\* Communicated by the Author.

are applied to the observed latitudes, so as to make the lengths of the corresponding divisions of the arc fit an ellipse; the same is done with all the other arcs brought to bear upon the problem; and then  $u$  and  $v$  (on which the sought-for semiaxes  $a$  and  $b$  depend) are found from the condition that the sum of the squares of all the above errors shall be an absolute minimum. In this process Bessel considers  $x$  to be an independent variable. It is in this that I think that he is wrong. I will now show why. Assuming  $x$  to be an independent variable amounts, as the process shows, to making the sum of all the corrections of latitude of the several stations of the arc equal to zero. Hence by this process  $x$  (the correction of the reference-station\* of the arc), with its sign changed, is equal to the sum of the relative corrections of the other stations of the arc divided by the whole number of the stations. No account whatever is taken of the error which may be produced at the reference-station by local attraction, which may be very large, so much so as to "overwhelm" other errors. Let  $t, t', t'', \dots$  be the deflections of the plumbline (reckoned positive when to the north) at the successive stations arising from local attraction. If the formulæ for calculating  $m, \alpha, \beta, \dots$  be examined (see 'Figure of the Earth,' p. 127, or Ordnance Survey, p. 737), it will be seen that the first term of  $m$  is the same as  $t' - t$ ; for (Figure of the Earth, p. 147, art. 149) the difference of deflection in the plane of the meridian at two stations equals the difference between the astronomical and mean amplitudes. Hence, denoting the remainder of  $m$  by  $h$ , the corrections which Bessel applies to the latitudes are

$$x, t' - t + h + \alpha u + \beta v + x, \dots,$$

in which  $h, \alpha, \beta, \dots$  are numerical quantities obtained from observed latitudes and measured arcs. In these corrections local attraction is taken account of in all of them except in that for the reference-station. For that station a mere arbitrary chance correction is applied; and if the local attraction there be large, the whole arc may be carried away by the "shifting" process, which Captain Clarke so clearly describes, to an inordinate dis-

\* I have called this both the "reference-station" and the "standard station" in my book. Captain Clarke observes that the latter is a term not known in geodesy. I am therefore quite willing to drop it. I made use of it for no special reason, and it is not desirable to multiply terms. He calls it the "initial point" (British Ordnance Survey, p. 738). I will retain "reference-station," as it so entirely represents the character of the station; for the position of the whole arc and its portions is determined by the observed latitude of that station, and by the observed amplitudes of the subdivisions from that station. Hence the whole is *referred* to that station.

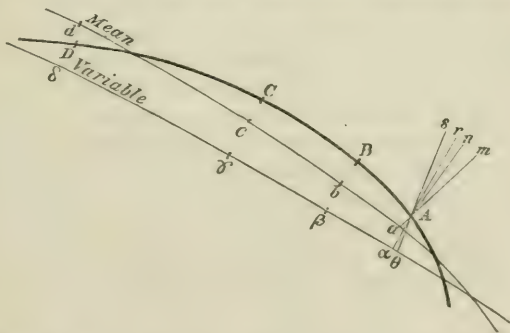
tance from its proper place. In fact, owing to the mere chance condition of the several divisions of the arc, the most important point of all (the reference-station) being left out of consideration, the Anglo-Gallic arc may be shifted one way, the Russian the other, and so of the rest; and the problem solved will be something of this kind, Given a certain number of pieces of curves, to find the nearest ellipse to which they can be made to belong, no restriction being imposed as to the parts of the ellipse to which they are respectively applied. This, of course, is not the physical problem which we have to solve; which is rather this, To find the nearest ellipse to which the several pieces of curves can be made to fit, the pieces all retaining their actual places.

3. The error, then, in Bessel's process is, I conceive, his treating  $x$  as an independent variable, which amounts to the same as his not taking into account the effect of local attraction in the correction  $x$  of the reference-station. It was to remove this defect that I published my method, which I will now describe.

## II. To explain my own method, as already published.

4. The first thing is to introduce a correction for local attraction. But there are no known means of determining its amount; all that is known is that it may be zero, or it may be, for all we know *à priori*, as much as (say)  $30''$ , more or less. Our ignorance of its amount is no excuse for leaving it out altogether; for it may have a very important effect. It must be some definite constant quantity at each station. Our only course is, therefore, to put an algebraical symbol, such as the constant  $t$ , to represent its amount.

Suppose  $A B C D$  is the measured arc, and  $a b c d$  is the mean ellipse; and let  $\alpha \beta \gamma \delta$  be any other ellipse near the mean ellipse,



and which I will call the variable ellipse. Let  $m A$  be the vertical at  $A$  in which the plumbline hangs,  $n A a$  a normal through

A to the mean ellipse;  $r A \alpha$  a normal through A to the variable ellipse;  $s A \theta$  a line through A making a small angle  $z$  with  $r A \alpha$ .

Now, if the earth had its mean form, the plumbline at A would hang in the line  $n A a$ , the normal to the mean ellipse. (N.B. As A does not coincide with  $a$  this would not be true, unless  $A a$  were a small quantity; but as it is small, the error in supposing the direction of gravity at A to coincide with the normal from A to the ellipse is of the second order, and may therefore be neglected.) But it actually hangs in the line  $m A$ . Hence the angle  $m A n$  is the deflection produced by local attraction at A, and equals  $t$ . The angle  $n A r$ , between the normals through A to the two ellipses,  $= n(v - V)$ , where  $n$  is a known quantity, and  $V$  the value of  $v$  for the mean ellipse (see 'Figure of the Earth,' p. 129). Hence by applying to the observed latitude of A the quantity  $t + n(v - V)$ —that is, the angle  $m A r$ , I make the point  $\alpha$  on the variable arc correspond with A on the actual arc, and the points  $\beta, \gamma, \delta$  are at the same distances from  $\alpha$  along the variable ellipse as B, C, D are from A along the measured arc. This, then, was the value which I gave to  $x$ , the correction of the latitude of A. I at first, however, added another correction still, viz. an arbitrary small angle  $r A s$  or  $z$ , with the same view for which Bessel used his  $x$ , viz. to adjust the small errors introduced by observation and measurement. In this case  $x$  would have equalled  $t + z + n(v - V)$ . But I had no sooner substituted this in the sum of squares of errors and differentiated with regard to  $z$ , than I perceived that the resulting formula would give me, not  $z$  alone (which I wanted), but  $z$  in inseparable company with  $t$ , thus  $t + z$ , and that therefore when I eliminated  $z$  I should be eliminating  $t$  also, and my end would be entirely defeated. Under these circumstances I felt obliged to leave out  $z$  altogether. The comparative fixity thus given to the arc  $\alpha \beta \gamma \delta$  on the variable ellipse I was aware of; and it is this which Captain Clarke objects to, and because of it, condemns my method of correcting Bessel's process, which he seems to think needs no correction. But the omission of this quantity  $z$ , which is sure to be very small, is not to be compared in importance with the omission of  $t$  (which Bessel's method omits), as  $t$  may be a comparatively large quantity. I do not think, therefore, that on a careful reexamination of the subject Captain Clarke will repeat his sentence, that I have "obscured" the matter, and that, in the sense in which he means, my calculation is "incorrect." I should rather turn the tables, and say that "the elements of the figure of the earth deduced by" Bessel's method, as he used it, "are, although they happen to be near the truth, arbitrary results founded on an incorrect calculation,"



which omits altogether the effect of local attraction at the reference-station. But I have now one step more to take.

### III. To suggest an Improvement of my Method.

5. I intend now to propose an improvement of my method which I think will correct, not only the larger defect of Bessel's, but also the smaller error which I have hitherto left uncorrected in my own. I will retain the correction  $z$ . It is necessary to frame an hypothesis regarding it in order to apply the principle of least squares. The hypothesis that  $z$  is an independent variable breaks down, as I have shown, and leads us into error. The hypothesis that  $z$  should have that particular form assigned to it which the principle of least squares suggests, viz. the average value, with its sign changed, of all the corrections of the several stations of the arc relatively to the reference-station and measured along the variable ellipse, also breaks down for the same cause;  $t$  is swept away from the equations when reduced; the measured arc, in fact, is allowed to shift away, as before, to a part of the ellipse to which it may not belong. It is necessary, therefore, to make some other hypothesis. I will give to  $z$  that particular value of the form above referred to which appertains to the mean ellipse; in short,  $z$  shall equal

$$- \frac{(m) + (\alpha)U + (\beta)V}{i},$$

a constant quantity. This hypothesis is free from the objections to the other two, and suits the problem.

This leaves the elaborate calculation in my paper in the Proceedings of the Royal Society, No. 64, untouched, except that  $z+t$ , a constant quantity, must be substituted for  $t$  in the formulæ.

6. In the case of the three arcs, the Anglo-Gallic, the Russian, and the Indian, I gather from Tables II. and I., p. 262 of that paper, and p. 270, that

$$\begin{aligned} z_1 &= - \frac{(m_1) + (\alpha_1)U + (\beta_1)V}{i} \\ &= - \frac{66.760 - 30.7150 \times 0.3581 - 12.3936 \times 0.8819}{34} = -1''.32, \\ z_2 &= - \frac{69.531 - 54.4933 \times 0.3581 - 15.9852 \times 0.8819}{13} = -2''.76, \\ z_3 &= - \frac{1.764 + 1.5836 \times 0.3581 - 2.6109 \times 0.8819}{8} = -0''.003. \end{aligned}$$

The three values of  $t$ , now to be called  $z + t$ , are found at p. 269 of the paper, and with the values of  $z$  give the equations

$$-1''\cdot32 + t_1 = -1''\cdot37, \quad -2''\cdot76 + t_2 = -2''\cdot22,$$

$$-0''\cdot003 + t_3 = -0''\cdot053;$$

$$\therefore t_1 = -0''\cdot05, \quad t_2 = 0''\cdot54, \quad t_3 = -0''\cdot05.$$

These are even smaller than those before obtained (I mean in the paper), and show that no one of the three reference-stations appears to be so situated (which might have been the case) as to have a large local attraction.

7. The three pairs of semiaxes deduced in the paper are, as there stated, remarkably near to each other in value; and therefore their mean, viz.

$$a = 20,926,189, \text{ and } b = 20,855,316 \text{ feet,}$$

may be taken, as before announced, to be the mean semiaxes of the earth.

8. The speculations regarding the constitution of the earth's crust, that it is such that we may conceive the elevations and depressions of the surface to have been caused by unequal contraction of the materials of the crust, remain as before, and appear to me well worthy of consideration.

Calcutta, May 7, 1866.

### III. *On the Regelation of Ice.*

By H. HELMHOLTZ.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

PROFESSOR HELMHOLTZ has forwarded to me the following Note, which forms an appendix to the translation of his excellent lecture upon glaciers, recently published in the *Revue des Cours Scientifiques*. You will, I doubt not, willingly give it a place in the *Philosophical Magazine*.

JOHN TYNDALL.

*To the Editor of the Revue des Cours Scientifiques.*

In reply to your question whether it is my desire to make any remarks on the new and ingenious experiments of Professor Tyndall, I would state that the results obtained with the swimming ice certainly show that, by very feeble pressure, pieces of ice may be caused rapidly to cling together. The pressures that come into play in this case are partly the difference in specific gravity between ice and water, and partly the capillary attrac-

tion exerted between two pieces of floating ice. It is to be borne in mind that, when in water, much more delicate ice-bridges suffice to connect two pieces of ice than when they are surrounded by air, where it is difficult to render the equilibrium so perfect as in water.

That radiant heat passing through ice melts the substance at points deep in the interior may be explained by assuming that at such places the ice-crystals have so crowded upon each other as to cause a pressure. If the water produced at such places be refrozen, the local pressure will be restored, and a new stream of heat will effect liquefaction at the same places, even when no free surface exists there.

According to Professor Tyndall's theory, the latent heat rendered free when two pieces of ice freeze together is conducted away through the adjacent ice. And as the difference between the freezing-points of the interior and superficial ice is certainly very small, the heat rendered sensible must diffuse itself through a comparatively large mass of ice if internal liquefaction is to be avoided. In view of the low conductive power of ice, and the extremely small differences of temperature, this seems to me improbable in cases where by a strong pressure, even by the stroke of a hammer, pieces of ice are welded together. I confess, however, that the time necessary for conducting away the heat cannot be subjected to exact calculation, and that therefore the question under discussion cannot yet be regarded as decided. For my own part I gave the theory of Mr. James Thomson the preference, because it bases itself exclusively upon well-known facts.

H. HELMHOLTZ.

IV. *On Hanging, considered from a Mechanical and Physiological point of view.* By the Rev. SAMUEL HAUGHTON, M.D., F.R.S., Fellow of Trinity College, Dublin\*.

**H**ANGING, as a mode of public execution of criminals, must be regarded as to a great extent an Anglo-Saxon mode of execution; and although occasionally practised by the nations of antiquity, it seems among them to have been used chiefly by suicides, or in cases in which especial ignominy was intended to be attached to the criminal.

Among the Hebrews, the national punishment was unquestionably that of stoning to death by stones thrown with the hand; and it is clear, from many passages in the Old Testa-

\* Communicated by the Author.

ment, that the hanging so often spoken of was the exposure of the body of the criminal, after death, to the birds of the air and to the beasts of the field, either by suspension from a tree, or by crucifixion on a gallows.

In Deut. xxi. 22, 23, it is provided that the criminal already executed shall be lifted up on a tree, and that his body shall be taken down before nightfall; it is also proved, by the story of the Hebrew thief in Herodotus, that the Jews, even before they left Egypt, had a special horror of the exposure of the dead at night to the birds of prey; for he relates that the King of Egypt exposed on a cross the headless body of the thief caught in the trap laid in the treasure-house, in the hope that his relations might be induced to attempt the removal of the body before nightfall.

From Gen. xl. 19, we may infer that the Egyptian practice was to execute the criminal by decapitation, and afterwards expose the body nailed on a cross to the birds of prey.

Among the Persians, also, exposure on a cross was a customary punishment, as appears from Esther vii. 9; but I do not know whether this crucifixion was post mortem or not; among the Hebrews, the "suspension" or "crucifixion" was always that of the dead body, and they were not guilty of the terrible atrocity of suspending or nailing up by the hands a living man: this refinement of cruelty was reserved for the Romans.

I have not succeeded in finding a case of execution by hanging in the Old Testament, although there are cases of suicidal strangulation (as that of Abithophel, 2 Sam. xvii. 23), which may have been effected simply by tying a cord round the neck, and have been unaccompanied by any "suspension," in the Anglo-Saxon use of the term.

The most ancient account of a formal execution by hanging that I can find is the hanging of the twelve faithless handmaids of Penelope at the suggestion of Telemachus, in the twenty-second book of the *Odyssey*. The passage is so remarkable for many reasons, that no apology is needed for offering some suggestions respecting it. I give the translation of Cowper, for the benefit of English readers.

" . . . . . leading forth

The women next, they shut them close between  
The lofty wall and scullery, narrow, straight,  
And dreadful, whence no prisoner might escape.  
Then, prudent, thus Telemachus advised:

The death of honour would I never grant  
To criminals like these, who poured contempt  
On mine and on my mother's head, and lay  
By night enfolded in the suitors' arms.



He said, and noosing a strong galley rope  
To a huge column, led the cord around  
The spacious dome, suspended so aloft,  
That none with quivering feet might reach the floor.  
As when a flight of doves entering the copse,  
Or broad-winged thrushes, strike against the net  
Within; ill rest, entangled, there they find;  
So they, suspended by the neck, expired  
All in one line together. Death abhorred!  
With restless feet awhile they beat the air,  
Then ceased."

Ὡς ἂρ' ἔφη, καὶ πείσμα νεὸς κυανοπρώροιο  
κίονος ἐξάψας μεγάλης περιβάλλε θόλοιο,  
ὑψόσ' ἐπεντανύσας, μήτις ποσὶν οὐδας ἵκοιτο.  
ὥς δ' ὅταν ἡ κίχλαι τανυσίπτεροι ἡὲ πέλειαι,  
ἔρκει ἐνιπλήξωσι, τόθ' ἐστήκει ἐνὶ θάμνῳ  
αὐλὴν ἐσιέμεναι, στυγερὸς δ' ὑποδέξατο κοῖτος,  
ὥς αἴγ' ἐξείης κεφαλὰς ἔχον, ἀμφὶ δὲ πάσαις  
δειρῇσι βρόχοι ἦσαν, ὅπως οἴκτιστα θάνοιεν  
ἥσπαιρον δὲ πόδεσσι μίνυνθά περ, οὔτι μάλα δῆν.

Od. xxii. 465-473.

There are two ways in which we may conceive the execution to have been effected.

1. Telemachus, with the aid of Eumæus and Philætiæus, having fastened one end of the rope to one of the main pillars of the hall, made slipknots (βρόχοι) upon it, which were placed round the necks of the twelve women, and having passed the other, or free end of the rope, round the top of the vaulted kitchen, they then all pulled together, in sailor fashion, on the rope, and hoisted the women into the air, so as to form a funicular polygon, in which some of them necessarily hung nearer to the ground than others—μήτις ποσὶν οὐδας ἵκοιτο.

2. The ship-rope, with one end fastened to the pillar, was carried round the vaulted dome of the kitchen (περιβάλλε θόλοιο) and made fast upon itself; from this rope were then suspended smaller ropes with slipknots or nooses (βρόχοι), which were passed round the necks of the women, who must have been lifted up one by one for the purpose, so as to swing clear of the ground. The simile of fieldfares\* and wood-pigeons caught in

\* It is a very remarkable confirmation of the minute accuracy with which Homer describes every phenomenon of nature, that fieldfares (*Turdus pilaris*) are now commonly caught by falconers as food for their hawks by a contrivance almost identical with that here described. A stick or rope is placed in front of either a hawthorne, or mountain ash, covered with berries, and from it are suspended running nooses at equal intervals. The

nooses hanging from a rope stretched from tree to tree, and placed in the passage to their roost, seems rather to favour the second interpretation, which is also aided by the words  $\acute{\omega}\varsigma \alpha\iota\gamma' \acute{\epsilon}\xi\epsilon\iota\eta\varsigma \kappa\epsilon\phi\alpha\lambda\acute{\alpha}\varsigma \acute{\epsilon}\chi\omicron\nu$ , as if the women hung, like Bluebeard's wives, "tit tat toe, all in a row!"

It can be shown, from mechanical considerations, that the first interpretation of this remarkable passage is not admissible; for, on the most favourable arrangement of the rope allowable, it would not have been possible for Telemachus, Eumæus, and Philætiüs, even if aided by the "man that bent the bow," and by the willing Euryclea, to have exerted the force necessary to lift all the women into the air together. The mechanical problem is also worth investigating for its own sake.

I shall assume, in order to simplify the conditions, that the women are hung at equal distances along the rope, and that the part of the rope joining the two lowest women is horizontal. These suppositions are very natural, and have the advantage of rendering the solution more elegant, without interfering seriously with its generality.

Let  $\alpha_1, \alpha_2, \dots \alpha_6$  denote the angles made by the several portions of the rope (reckoned from the top) with the horizon.

Let  $T_1, T_2, \dots T_6$  denote the strain on each portion of the rope.

Let  $T_7 = X$  be the strain on the lowest or horizontal portion of the rope.

Let  $W$  denote the weight of one of the women.

As the second half of the rope is supposed to be symmetrical for the present, there are thirteen unknown quantities to be found, viz. the six angles and seven tensions. From the well-known principles of equilibrium of the funicular polygon, we obtain the following twelve equations, which are all *mechanical*:—

$$T_1 \cos \alpha_1 = T_2 \cos \alpha_2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$T_2 \cos \alpha_2 = T_3 \cos \alpha_3, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$T_3 \cos \alpha_3 = T_4 \cos \alpha_4, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$T_4 \cos \alpha_4 = T_5 \cos \alpha_5, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$T_5 \cos \alpha_5 = T_6 \cos \alpha_6, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$T_6 \cos \alpha_6 = T_7 = X. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

fieldfares ( $\kappa\acute{\iota}\chi\lambda\alpha\iota \tau\alpha\nu\nu\sigma\acute{\iota}\pi\tau\epsilon\rho\omicron\iota$ ), in trying to fly at the berries, are stopped by their broad wings in passing through the nooses, and are so caught by the neck, or occasionally by the foot, but most frequently by the neck; and the stratagem is so successful with this bird, that they are often found hanging in a row from the stick, each suspended by the noose that passes round his neck.

$$T_1 \sin \alpha_1 = T_2 \sin \alpha_2 + W, \quad . \quad . \quad . \quad (7)$$

$$T_2 \sin \alpha_2 = T_3 \sin \alpha_3 + W, \quad . \quad . \quad . \quad (8)$$

$$T_3 \sin \alpha_3 = T_4 \sin \alpha_4 + W, \quad . \quad . \quad . \quad (9)$$

$$T_4 \sin \alpha_4 = T_5 \sin \alpha_5 + W, \quad . \quad . \quad . \quad (10)$$

$$T_5 \sin \alpha_5 = T_6 \sin \alpha_6 + W, \quad . \quad . \quad . \quad (11)$$

$$T_6 \sin \alpha_6 = \left\{ \begin{array}{l} T_7 \sin \alpha_7 \\ = 0 \end{array} \right\} + W. \quad . \quad . \quad . \quad (12)$$

The twelve unknown quantities in these equations, which denote the inclinations and tensions of the first six portions of the rope, may be all expressed as follows, after a few reductions, in terms of  $X$ , the horizontal strain on the funicular polygon :—

$$\left. \begin{array}{ll} T_1 = \sqrt{36W^2 + X^2}, & \tan \alpha_1 = \frac{6W}{X}, \\ T_2 = \sqrt{25W^2 + X^2}, & \tan \alpha_2 = \frac{5W}{X}, \\ T_3 = \sqrt{16W^2 + X^2}, & \tan \alpha_3 = \frac{4W}{X}, \\ T_4 = \sqrt{9W^2 + X^2}, & \tan \alpha_4 = \frac{3W}{X}, \\ T_5 = \sqrt{4W^2 + X^2}, & \tan \alpha_5 = \frac{2W}{X}, \\ T_6 = \sqrt{W^2 + X^2}, & \tan \alpha_6 = \frac{W}{X}. \end{array} \right\} . \quad . \quad (13)$$

If  $a_1, a_2, a_3, a_4, a_5, a_6$  denote the lengths of the six portions of the rope, we obtain, from *geometrical* considerations, the following equation :—

$$\left. \begin{array}{l} a_1 \cos \alpha_1 + a_2 \cos \alpha_2 + a_3 \cos \alpha_3 + a_4 \cos \alpha_4 + a_5 \cos \alpha_5 \\ + a_6 \cos \alpha_6 = \text{const.}, \end{array} \right\} . \quad (14)$$

in which equation the constant depends on the span of the polygon from the pillar of the hall to the top of the vaulted kitchen.

If we were to substitute in equation (14) the values of the cosines of the angles found from (13), it would become an equation ultimately of a high degré, the real root of which would give the solution of the problem sought ; but it is not necessary to trouble ourselves with this equation, as we know that the value of  $X$  must be real and positive, and by (13) we have

$$T_1 = \sqrt{(6W)^2 + X^2}.$$

In this equation  $T_1$  denotes the pull on the rope that Telema-

chus and his assistants must have used in order to hold up the free end of the funicular polygon; and since  $X$  is real, the value of  $T_1$  will always be greater than the weight of six of the handmaids, and will be considerably greater, unless the heights of the points of suspension be very great compared with the span of the polygon. We are therefore forced to the conclusion that the hanging of Penelope's handmaids in a funicular polygon was mechanically impossible, unless pulley-blocks or some other contrivances were employed, which are not mentioned in the text. We must therefore suppose that in this, the earliest execution by hanging on record, the rope was passed around the vaulted dome, and that separate nooses suspended from this rope were attached to the necks of the women.

In modern times hanging was a favourite mode of execution among the Anglo-Saxons; and I am indebted to Dr. Ingram, Professor of English Literature in the University of Dublin, and to J. E. Walshe, Q.C., for the following brief notice of its history in connexion with England, which will serve as a suitable introduction to my proposal for its improvement and perfection, founded on mechanical and physiological principles.

Hanging was only one of the capital punishments in use among our ancestors—women being often burned for offences for which men were hanged, and both were burned for holding heretical opinions. Marrying a Jew or committing sodomy was at one time punishable by burying both parties alive; and beheading with an axe was, and theoretically still is, allowable in some cases. The punishment for high treason, and at one time extended to certain cases of murder, was the elaborate and brutal process of hanging, drawing, and quartering.

In "*Beowulf*," which Kemble believed to be a modernized form of a poem which the invaders of Britain had brought with them from their continental homes, the gallows (*galya*) figures as an old-established institution of the Teutonic races of Northern Europe.

It is mentioned by Blackstone as a somewhat singular fact, that the only warrant the sheriff has for a capital execution is the signature of the judge to the calendar, or list of all the prisoners' names, with their respective judgments in the margin.

"As for a capital felony, it is written opposite to the prisoner's name 'hanged by the neck,' formerly in the days of Latin and abbreviation 'sus. per col.' for 'suspendatur per collum.'"

Originally there was a formal precept to the sheriff under the hand and seal of the judge; but the form of it is not given in the law books, nor is it certain how long the formula now employed in sentencing a criminal ("hanged by the neck till you are dead") has been employed.



“It is clear,” says Blackstone, “that if upon judgment to be hanged by the neck till he is dead the criminal be not thoroughly killed, but revives, the sheriff must hang him again.” But, strangely enough, we find in the ‘*Vision of Piers Plowman*,’ a passage which seems to show that the opposite of this either was, or was believed to be, the established rule in his time:—

“It is noght used on Earthe  
To hangen a felon  
Ofter than ones,  
Though he were a tretour.”

From some cause or other, not easy to explain, it has been the custom to use a longer drop in Ireland than in England or Scotland; and there can be no doubt that it is a more humane mode of execution than the English, and also more instructive as a solemn warning to the spectators, whose feelings are not likely to be enlisted on the side of the criminal by witnessing his convulsive struggles, which are an unnecessary accompaniment of death by hanging if properly conducted. On a recent occasion in the north of England, the criminal had undergone tracheotomy some years previous to his execution; and such was the ignorance of those who conducted the hanging, that he was dropped through a short height quite insufficient to injure the spinal cord, and breathed with ease through the aperture in the trachea, suffering horrible tortures, until relieved by the humanity of the surgeon of the jail, who closed with his finger the aperture through which he breathed, and so completed the clumsy work of the hangman.

In using the long drop, also, mistakes may occur, either through the weakness of the rope, or through miscalculation of the length of the drop. Both these errors were exemplified at Castlebar in Ireland in 1786, at the execution of the notorious George Robert Fitzgerald, who, when he jumped off the ladder, broke the rope; and when he was hanged the second time the rope was too long and his toes touched the ground, until at length a humane bystander raised him up while the hangman shortened the cord.

Death is produced by hanging in one or other of the three following ways:—

1. By apoplexy, caused by pressure on the jugular veins;
2. By asphyxia, caused by stoppage of the windpipe;
3. By shock of the medulla oblongata, caused by fracture of the vertebral column.

In the first two cases death is preceded by convulsions, lasting from five to forty-five minutes, which are caused by the cessation of the supply of arterial blood to the muscles. In the third case death is instantaneous and painless, and is unaccompanied by any convulsive movement whatever.

According to the original form of death-punishment for treason in England, the hanging was used as an anæsthetic, preparatory to the disembowelling (or drawing) that always preceded the quartering of the criminal; and the present slow process of hanging practised by Calcraft and others in England and Scotland, which consists in dropping the patient through three or four feet and allowing him to hang until dead, is the faithful representation of the original process of hanging, which was intended to fulfil a purpose quite distinct from that of speedy execution of the criminal.

It seems to me unworthy of the present state of science to continue a mode of execution which, as at present used, is extremely clumsy and also painful to the criminal. Instead of the "short drop" generally used, we ought to employ the "long drop," which causes instantaneous death. It has been ascertained by me that the shock of a ton dropped through one foot is just sufficient to fracture the anterior articulating surfaces of the second vertebra at their contact with the atlas; and that this fracture allows the shock to fall upon the medulla oblongata so as to produce instantaneous death. As the result of some consideration bestowed upon this subject, I would recommend the adoption of the following rule:—

*Rule I.* "Divide the weight of the patient in pounds into 2240, and the quotient will give the length of the long drop in feet."

For example, a criminal weighing 160 lbs. should be allowed 14 feet drop. If local circumstances will not allow of the long drop being employed, the requisite shock should be produced by strapping a shot to the feet, so as to secure the shock of 2240 foot-pounds to the medulla.

Efforts have been made in the United States to give to hanging all the rapidity of death by the guillotine without the painful spectacle of bloodshed. This method, which is borrowed from the mode of execution practised on board ship, consists in suddenly lifting the criminal into the air by means of a great weight attached to the other end of the rope fastened round his neck; the rope passes over a pulley placed vertically over the patient, and at a given signal the weight falls through a regulated height, lifting him suddenly into the air. Sufficient attention, however, has not been paid, even in that enlightened country, to the conditions necessary to be fulfilled in this mode of suspension; for in many of their executions, the only care that seems to have been taken was to make the falling weight heavier than the criminal, so as to ensure his permanent suspension by the neck until death terminated his sufferings.

The American method of hanging, if properly applied, seems

to me to be capable of producing death by shock with even less suffering than the "long drop;" for although by the latter method death is instantaneous when the shock actually occurs, yet the mental sufferings of the criminal during the second occupied by his fall may be very considerable. This painful interval is altogether avoided in the American method, provided the *initial* shock be sufficient to destroy the medulla oblongata. This important condition may be effected by the following calculations, which lead to an easy Rule.

The falling weight, acting through the intervention of the rope, produces its effect in a manner similar to that of the shock or collision of imperfectly elastic bodies.

Let  $m$  and  $m'$  denote the masses of the two bodies, and let  $v$  and  $v'$  denote their velocities previous to collision or shock, while  $e$  denotes the coefficient of elasticity of the rope.

Let  $u$ ,  $u'$  denote the velocities of the masses  $m$ ,  $m'$  after the shock; then it is well known\* that

$$\left. \begin{aligned} u &= \frac{mv + m'v' - em'(v - v')}{m + m'}, \\ u' &= \frac{mv + m'v' - em(v' - v)}{m + m'}. \end{aligned} \right\} \quad \dots \quad (15)$$

The *vis viva* lost during the shock is expended upon the neck of the criminal, and is represented by

$$mv^2 + m'v'^2 - mu^2 - m'u'^2.$$

After some reductions this is found to be

$$\text{vis viva lost} = \frac{mm'}{m + m'}(1 - e^2)(v - v')^2. \quad \dots \quad (16)$$

This result may be applied practically to the solution of the American problem of hanging, so as to cause instantaneous death, in the following manner.

Let  $P$  denote the weight employed, and  $Q$  the weight of the criminal; let  $e$  denote the coefficient of elasticity of the rope used, and  $v$  the velocity acquired by the weight  $Q$  in falling through the height  $h$ .

If we consider the problem of the weight  $Q$  moving with the velocity  $v$ , and causing the weight  $P$  to move through the intervention of the rope whose elasticity is  $e$ , the shock produced on  $P$  at the moment when the "chuck" takes place is similar to that which occurs in the collision of bodies striking each other, and is measured by the *vis viva* lost during their collision. The

\* Vide 'Manual of Mechanics,' p. 156.

32 The Rev. S. Haughton on *Hanging, considered from vis viva* lost during the shock is (16)

$$\frac{1}{g} \cdot \frac{PQ}{P+Q} (1-e^2)v^2;$$

but since the *work lost* is half the *vis viva lost*, if we substitute for  $v^2$  its value,  $2gh$ , we find

$$\text{work lost} = \frac{PQ}{P+Q} (1-e^2)h. \quad (17)$$

For the ropes usually employed,  $e$  may be regarded as a very small fraction, and  $e^2$  may be totally disregarded. The *work lost* is expended in causing shock to the neck, and should therefore be equal to at least 2240 foot-pounds.

In a case of hanging that came under my own observation, the criminal weighed 160 lbs., and was allowed to fall through 14 feet 6 inches, which, allowing for some elasticity in the rope, would correspond with 2240 foot-pounds of shock; in this case the superior articulating surfaces of the second vertebra were fractured near their posterior border (the fracture of the bone extending to the foramina for the vertebral arteries), but the odontoid process and its transverse ligament were so strong that neither of them was injured. Death in this case was as instantaneous as it would have been had the transverse ligament given way instead of the bone; for the shock reached the medulla, and its consequence was immediate and painless death. In hanging, the rope supports the atlas and presses it against the occipital articulations, while the second vertebra tends to fall with the body; and it follows from this, that either the odontoid process and its transverse ligament must give way, or the second vertebra be broken across at its superior articulating surfaces; in either case death will be immediate. The height of the criminal just mentioned a few days before execution was 5 feet 9½ inches, and after death he was found to measure 5 feet 11 inches; having been elongated by 1½ inch by the "long drop" of 14½ feet.

From the foregoing it therefore appears that a shock to the neck of 2240 foot-pounds is just sufficient to cause immediate death; substituting, therefore, 2240 foot-pounds for the work lost in the preceding equation, we find

$$2240 = \frac{PQh}{P+Q},$$

or, solving for  $P$ ,

$$P = \frac{2240Q}{Qh - 2240}. \quad (18)$$

From this equation it follows that, unless  $Qh$  be greater than



2240, the value of  $P$  (the weight required) will be negative; but  $Qh$  denotes the work produced by the criminal  $Q$  falling through the height  $h$ .

Let  $h$  therefore denote the "long drop" found by Rule I., and the following consequences may be inferred from (18).

1st. In the American mode of hanging, if the weight be let fall through the height  $h$ , sufficient to cause death instantaneously by the "long drop," it would require an infinite weight to cause immediate death; for in this case

$$Qh - 2240 = 0,$$

and therefore  $P$  is infinite.

2nd. In the American mode of hanging, if the weight be let fall through twice the height of the "long drop," a weight equal to that of the criminal will be sufficient to cause immediate death; for in this case

$$Qh - 2240 = 2240,$$

and therefore, by equation (18),

$$P = Q.$$

For all heights intermediate between  $h$  and  $2h$ , the weight  $P$  must be found from equation (18), and it will always lie between  $Q$  and infinity.

In practice, twice the height of the "long drop" would always be found convenient; and therefore the following Rule for producing instantaneous death by the American method is confidently recommended.

*Rule II.* "Having found from Rule I. the height of the Irish long drop, use twice this height, and a weight equal to that of the criminal, in the American method.

*Note.*—I have searched in vain for well-authenticated instances of fracture of the cervical vertebræ produced by the usual method of hanging. Among the longest drops that I can find recorded, are two observed by Dr. Charles Croker King, when Professor of Anatomy in the Queen's College, Galway.

*Case I.\** A young man, named Hurley, was executed in Galway, at 6.25 P.M. on the 27th of August, 1853, for the murder of a young woman in Dunsandle Wood. The rope used was 10 lines in diameter; the knot was large, formed of three turns of the rope, and, on the noose being tightened by the executioner, corresponded to the occipital protuberance. His weight was  $10\frac{1}{2}$  stone, and he was allowed a drop of  $7\frac{1}{2}$  feet. These data give us as follows:—

$$\text{work done} = 147 \times \frac{15}{2} = 1102 \text{ foot-pounds.}$$

\* Dublin Quarterly Journal of Medical Science, vol. xviii. (1854) p. 86 et seq.

In this case, as Dr. King remarks, "there was no dislocation or fracture of the vertebral column, or injury of the ligaments or of the spinal cord."

*Case II.\** On the 11th of May, 1858, Patrick Lydon was hanged in Galway for the murder of his wife. Lydon was a small man, only 5 feet 5 inches in height; the diameter of the rope was 10 lines; his weight was  $9\frac{1}{2}$  stone, and the drop 11 feet. Hence we find

$$\text{work done} = 133 \times 11 = 1463 \text{ foot-pounds.}$$

In this case, "that portion of the anterior common ligament of the spine which passes from the body of the second to that of the third cervical vertebra was ruptured, so that the left halves of the bodies of the above-mentioned vertebræ were separated from each other by an interval of one-eighth of an inch, but there was no displacement."

These criminals were executed with the same rope, and death in the second case was not preceded by violent muscular convulsions, as in the first case—a fact which is readily accounted for by the excess of shock in the proportion of 1463 to 1102.

### V. On the Problem of Sea-levels.

By D. D. HEATH, M.A., F.G.S.†

**I**N a paper published in March last, I investigated the question recently mooted among geologists as to the effect of an ice-cap, or other accumulation of superficial matter, in locally altering the mean sea-level.

I was more familiar with the formulas required than with Laplace's mode of using them; and I partly misunderstood and misapplied his method. My labour was not, however, wasted; for I had rightly deduced the external form, or contour-line, which a sea covering a denser solid spherical nucleus would assume under the influence of an external capping supposed to be anyhow kept at a definite distance apart from it. My error lay in arguing that, when the agency keeping them apart is a solid connexion between the cap and the nucleus, this nucleus will, to the first order of small quantities, lie centrally within the envelope.

This error I corrected in April, and explained that the centre of the solid sphere will be, as it were, depressed by the superincumbent weight of the cap, and lie away from the centre of figure in the opposite direction by a distance of the same order of mag-

\* Dublin Quarterly Journal of Medical Science, August 1863.

† Communicated by the Author.

nitude, generally speaking, as that of the ellipticity of the surface. Taking my former illustration, the *yolk* of the egg will lie on the big-end side of its centre of gravity.

In applying this theory to facts, we must conceive our continents and islands as so many excrescences from the spherical nucleus which will shift their positions along with it; so that the change of level, as measured on a cliff or mountain, will be that calculated in my first paper, due to the change of contour, increased in one hemisphere and diminished in the other by an amount proportional to the sine of the latitude, the change at the equator being due to the former cause only. To complete the theory, each of these excrescences must be treated as exerting a disturbing force of the same kind as the supposed ice-cap, and all the effects must be added together.

In the same April Number there was a paper by Mr. Croll, in which he criticised my uncorrected paper, and also developed his own theory; and he appended a note by Professor W. Thomson, expressing a marked approval and acceptance of this theory, as including all that is relevant to "the great physical question."

As to the first part of Mr. Croll's paper, I have only to say that, were I rewriting my own, I should leave out my illustration of his axiom by reference to the moon, but should retain that by the sun. But if, as I imagine, he thinks that, were the moon stayed in her motion and rigidly connected with the earth, the water would tend to gather spherically round the common centre of gravity, he is wrong. The sea would keep the elliptic shape assigned to it by the common statical theory of the tides, but the nucleus would be removed some 85 feet from the centre of the ellipse\*; whereas the common centre is 3000 miles off.

As to Mr. Croll's own theory, perhaps the fault is mine, but certainly I and Professor Thomson read it differently.

For Professor Thomson concludes with the very just remark—obvious I should have thought it, but that Archdeacon Pratt seems to include *floating* ice in his disturbing force (p. 174)—"that a transference of floating ice goes for nothing; and that in estimating the effect of *grounded icebergs*, the excess of the mass of ice above that of the water displaced by it is to be reckoned just as if so much ice were laid on the top of an island." Now on looking more closely into Mr. Croll's theory (which I had only glanced at in the 'Reader'), I see that his ice-cap is supposed to be fitted to a lens-shaped nucleus at the bottom of the sea with a mile or two of water flowing over it! (p. 302 at bottom, and both the figures).

\* In my notation,  $\delta : a :: \frac{\text{mass of moon}}{(\text{distance})^2} : \frac{\text{excess of mass in nucleus}}{a^2}$ .

This explains, perhaps, how he came by the proposition to which I have objected. For one of Laplace's theorems is that, when a nearly spherical nucleus is everywhere covered by a fluid envelope, the centres of gravity must coincide.

But not only is this hypothesis quite irrelevant to the physical facts, but it utterly vitiates the whole reasoning. If we neglect the difference of density between ice and water, it is perfectly indifferent to equilibrium how much of the sea becomes ground-ice; and if we take it into account, the ground-ice gives buoyancy instead of weight to the attached nucleus, and will disturb equilibrium in the sense opposite to that assumed by Mr. Croll. In his imaginary case, introduced for illustration, of a nucleus of the same density as ice, no position will be stable but with the solid partly out of water. I need not say that this is not the theory which Professor Thomson has really adopted in his own solution of the problem. And in truth he only throws a student off the scent by directing him to "work according to Mr. Croll's directions." What he really does, in substance, is this.

He borrows from Mr. Croll the conception of an ice-cap extending down to the equator, and substituting (as I and other followers of Laplace have done) density for thickness, he supposes the density to vary as the cosine of the polar distance; which represents the law of thickness in Mr. Croll's meniscus when in its vanishing state. This being so, if we start with a southern glacial epoch, and suppose the hemispherical shell to represent the excess of southern over any then existing northern ice, then a northern epoch, or the exact reversal of this state of things, may be represented by the superposition upon it of a *complete* spherical shell, following the above law with reversed pole; *i. e.* having a negative density southward, which will neutralize the southern cap, and a positive density at the north.

Such a shell will be found to exert on all points within it equal and parallel forces directed northward. It will therefore produce no effect on the contour, but will displace the moveable fluid until the excess of matter in the nucleus balances the northerly, as it formerly balanced the southerly attraction of the hemispherical shell at the centre of figure.

This gives in my notation a displacement  $\frac{\beta}{\rho-1}$ , which in Professor Thomson's would be  $\frac{it}{1-\omega}$ . But he introduces the consideration of the supports of the ice-cap as islands equably distributed over the globe, on which alone he supposes the ice to rest. This makes the *average* thickness of ice covering any zone of latitude proportional to  $(1-\omega)it$ , and the proportion of fluid matter



relatively displaced from one epoch to the other  $\omega w$  instead of  $w$ .

Hence his formula  $\frac{(1-\omega)it}{1-\omega w}$ .

It does not belong to me to praise the neatness of Professor Thomson's work; but I must remark upon his observation that the first term in Laplace's series "always expresses the *essence* of the result," and also upon the applicability of his solution to the actual geological question.

He cannot mean that in every case where Laplace's methods can be used the first term is of a higher order of magnitude than the sum of all the subsequent terms. I suppose, therefore, that he must mean to lay it down that in the passage from one set of disturbing forces to an approximately equal and opposite state—as from a southerly to a northerly epoch—this will be the case.

I appeal to my calculation of a special case to show that this is not so. With a uniform cap extending to N.P.D.  $30^\circ$ , I find the total displacement at the pole is  $1078 + 206$ , or  $1284$ , of which the part due to the shifting of the centre is  $750$ .

And if we look to the *rationale* of the thing, it is evident that the peculiar result he has come to implies that, with that special law of thickness and extension of the capping, the form assumed by the surface is symmetrical in the two hemispheres, or, which is the same thing, that its equation, referred to an origin near the centre of figure (such as the centre of the nucleus), is of the form  $r - a = a \{ \alpha_1 Q_1 + \alpha_2 Q_2 + \alpha_4 Q_4 + \&c. \}$ , with no odd terms after the first: and this is easily verified\*. But when the form is unsymmetrical and other odd terms appear in the equation, then the change of level, referred to the same origin, in passing from this state to its opposite, is due to the shifting both of the contour-line and of the centre of figure; and the relative amounts at the pole are as the sum of the coefficients of all the odd terms after the first to that of the first.

\* Referring to my March paper, it will be seen that when the density varies as  $\mu'$ ,  $\alpha_n a$  will be a multiple of  $\int Q'_n \mu' d\mu'$  between proper limits. Now

$$n(n+1)Q_n = - \frac{d}{d\mu} \left\{ (1-\mu^2) \frac{dQ_n}{d\mu} \right\}.$$

Whence, multiplying by  $\mu$  and integrating by parts, it will be found (when  $n > 1$ ) that

$$(n-1)(n+2) \int Q_n \mu d\mu = C - (1-\mu^2) \left( \frac{dQ_n}{d\mu} - Q_n \right).$$

Taken from any given latitude to the pole, this becomes

$$(1-\mu_1^2) \left( \frac{dQ_n}{d\mu_1} - Q_n \right);$$

and when we start from the equator it reduces to  $-Q_n$ , which vanishes when  $n$  is odd.

But even if this were otherwise, I apprehend the question which geologists are now putting is not to be answered by merely calculating the difference between two approximately similar and opposite states. They want to know whether any conceivable glaciation in the northern hemisphere would raise the sea in the latitude of North Wales by 1000 or 2000 feet *above its now existing level*. Surely, with the excentricity of our orbit, I believe, near its *minimum*, we are not now in a state of extreme southern glaciation! If we are, the whole astronomical theory of glacial epochs falls to the ground; and, moreover, though I suppose there may be sensibly more ice now in the south than in the north, no one can imagine that the *difference* is enough to produce any sensible change of level.

My investigation has the disadvantage of resulting in a series, whence it is not easy to deduce general propositions; but it is addressed to the actual question.

Archdeacon Pratt has also given a solution of the problem in the March Number of the Magazine. If it could be accepted as it stands, or if it admits of correction, it possesses the advantage of being expressed in few terms, though it is liable to the objection that, like Professor Thomson's, it supposes the capping to reach to the equator.

But I must confess, with some diffidence, that it appears to me radically erroneous.

It is a corollary from his 'Figure of the Earth,' with which I have only become acquainted in consequence of the paper's references; and I must admit that the objections I have to urge against the paper are equally applicable to a large section of the more permanent work. I will, however, endeavour to make them intelligible to those who have only the Magazine before them.

The fundamental equation (1), p. 173, is an empirical formula, the coefficients being determined by making it approximately represent the attractions on points in four latitudes,  $0^\circ$  and  $30^\circ$ ,  $45^\circ$  and  $60^\circ$  south, which four attractions are to be previously computed "by the reader" with the help of certain Tables. I have not had the courage to verify the calculations; but taking them as data, I find that the formula (1) is made to represent three of them exactly; and then the remaining one comes out  $\cdot 122$  instead of  $\cdot 412$ , which is perhaps near enough to give us confidence in applying it to other southern latitudes.

But it fails in the northern hemisphere. The Archdeacon has, if I am not mistaken, exaggerated the divergence. For the expression  $0\cdot6 \sin 2\phi$ , *e. g.* (p. 173) seems to be that for the attraction of a homogeneous spheroid of the same density with the earth; whereas he uses it for one of the density  $2\cdot75$ , or about half that of the earth.

Still, even when corrected, we are thus presented with a discontinuous expression of the attraction exerted by the disturbing force on points of the ocean's surface. And this seems to me a formidable obstacle to dealing with the problem in the only way I think admissible, and which the Archdeacon himself at first propounds (*Figure of the Earth*, p. 155), viz. by endeavouring to satisfy the equation (in which I leave out the term for the centrifugal force as immaterial)

$$\int_p \frac{dp}{p} = V + \int U du = \text{const.},$$

where  $V$  is the *internal* potential, and  $\int U du$  that due to the disturbing force.

I conceive it would be necessary to assume a form of surface, with indeterminate coefficients, having the same discontinuous passage from one hemisphere to the other, thence to calculate  $V$  to the same order of small magnitudes as  $\int U du$ , then to determine the coefficients so as to satisfy the equation at all parts of the surface, and finally to determine the constant of integration so as to ensure the permanence of the mass of water in the disturbed and undisturbed spheroid.

But Archdeacon Pratt proceeds to assume for  $V$  its value in the undisturbed spheroid,—a liberty which may be justifiable in the case of an isolated sea like the Caspian, in which any sensible effect of an overhanging table-land or mountain-range would probably overwhelm that due to any possible change of surface of the sea, but which seems to me wholly illegitimate when we are dealing with an ocean covering three-fourths of the globe, which can and will adapt itself to the new forces.

But having thus obtained, however wrongly, his equation to the disturbed surface, viz.

$$\frac{a}{r} = 1 + \epsilon \mu^2 - \frac{a}{E} \int U du,$$

he does not proceed to determine the constant of integration so that the mass may remain unaltered, but he goes through a calculation which is equivalent to the following:—

If  $R$  be the radius of the undisturbed surface

$$\frac{a}{R} = 1 + \epsilon \mu^2,$$

whence, subtracting and transforming,

$$r - R = \frac{Rr}{E} \int U du = \frac{a^2}{E} \int U du, \text{ or } \frac{1}{g} \int U d\iota, \text{ nearly.}$$

And from this he infers that the "whole elevation of the sea-level," *i. e.* the value of  $r - R$ , is the integral  $\frac{1}{g} \int U du$  "between the proper limits." (Phil. Mag. p. 174.)

But for these "proper limits" he, without reason or warrant, takes the equator and the latitude where he wants to ascertain the submergence; whereas he ought to take it from the point where the disturbed and undisturbed surfaces coincide, which he has never determined.

If I may venture on a conjecture, it is from mistrust of the assumption "that the attraction of an elementary prism of the superficial matter may be treated as concentrated in one point of its length"—the same, approximately, whether the attracted particle is under, near, or distant from it—that Archdeacon Pratt has adopted his peculiar method and got hold of his discontinuous formulas. This may require a closer investigation; but I believe the objection is unfounded as applying to the determination of the general figure of the ocean. It may be valid as regards a small margin on either side of the latitude at which the capping terminates abruptly; but not, I think, as regards points fairly under the capping or fairly away from it. I will not attempt here to go further into the question. If that assumption (which I have distinctly made) must be abandoned, we must hope that Archdeacon Pratt will be able to remove objections and complete his own theory.

I will conclude with an observation of a physical character, though I have hitherto kept entirely to the mathematical theory of attractions.

I have taken a uniform thickness of ice: others have supposed it to thin out in lower latitudes, according to whatever law they found convenient for their calculations. I think it essential that those calculations should not depend for their validity on the cap reaching down to the equator. But, this once secured, it may at first sight appear that a law of thinning out must be nearer to the case of nature than that of uniform thickness. But I doubt whether it is so. Within certain limits of climate, I apprehend the real cause determining the thickness will be the distribution of land and shallow seas; and that you cannot have more than a certain depth of ice heaped up on a given area, island or shoal. It will crack away, or ultimately be crushed by its own weight, and float away in powder, flakes, or icebergs, into seas of lower latitudes.

Kitlands, Dorking.



VI. *On the Reflection of Light in the Atmosphere.*

By Professor R. CLAUSIUS.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

**I** NOTICE in the Proceedings of the Royal Society for February an interesting communication by Messrs. Roscoe and Baxendell "On the Relative Chemical Intensities of direct Sunlight and diffused Daylight at different Altitudes of the Sun," in which my theoretical investigations on the dispersion of light in the atmosphere are mentioned. May I be permitted to communicate a few observations to which this paper have led me?

From calculations made partly by themselves and partly by M. Wolkoff in Heidelberg, the authors have deduced the ratio between the chemical intensities of direct sunlight and of diffused daylight. The values thus obtained they have collated in the following Table, with the results of a calculation which I made under the supposition that the reflection of light in the atmosphere is occasioned by vesicles of water\*.

Sun's altitude.	Calculated (Clausius).	Experiments.		
		Heidelberg.	Cheetham Hill.	Owens College.
20°	0.491	0.35	0.19	0.10
25	0.896	0.48	0.20	0.11
30	1.320	0.65	0.23	
35	1.690	0.82	0.26	
40	2.032	1.00		
50	2.634	1.37		
60	3.129	1.60		

As the numbers in the column "calculated" do not agree with the numbers deduced from experiments†, they conclude hence "that the effect of the atmosphere upon the highly refrangible and chemically active solar rays is regulated by totally different laws from those founded upon the hypothesis of the reflection by means of hollow vesicles of water."

\* Crelle's *Journal*, vols. xxxiv. and xxxvi.; Poggendorff's *Annalen*, vol. lxxii. p. 294.

† I must here remark that an error occurs in this Table. I have determined the position of the sun by giving its zenith-distance; and in the Table the numbers which refer to the zenith-distances 80°, 75°, 70°, &c., are given as if they referred to the sun's heights 20°, 25°, 30°, &c., instead of to the heights 10°, 15°, 20°, &c. If this confusion had not arisen, the differences between the calculated and observed values would have been greater than the Table shows.

I cannot admit that this conclusion is correct ; for the numbers resulting from my calculation cannot be used in the sense in which they have here been taken, but the comparison of observation with theory must be made in a totally different manner.

In adducing my numbers I have expressly stated\* that they do not simply depend upon the hypothesis that the reflection is occasioned by the vesicles of water, but that in calculating them, several other assumptions have been made, of which I may mention the following as the most important. In my general formulæ a coefficient occurs which depends on the degree of transparency of the atmosphere. This coefficient may at different times and in different places have very different values, since even when the sky is supposed to be cloudless (which is the case in the formulæ) the degree of transparency may vary considerably. Hence the coefficient must be especially determined for each series of observations which is to be compared with the results of theory. At the conclusion of my paper I have even said that this coefficient must be different for different kinds of rays, since the atmosphere does not transmit rays of all colours with equal facility. It is well known that the blue rays of the atmosphere are less readily transmitted by the atmosphere than the red ones ; and it must therefore be assumed that the chemically active rays, which are even more refrangible than the blue ones, must be still less readily transmitted than these. In the *numerical* calculation which I have carried out, to give an example of the application of the general formulæ, I have chosen a value for the coefficient which has been obtained from observations on radiant heat as an approximate mean ; but this value is not to be regarded as universally applicable.

If in a theoretical determination of the luminous intensities in the atmosphere all cooperating circumstances are to be taken into account, the calculation becomes very tedious, and I shall therefore restrict myself to an approximation.

The quantity of light which a horizontal unit of surface of the earth would receive from the sun, if the sun were in the zenith and there were no atmosphere, may serve as unit. Taking, then, the sun at any given height  $\vartheta$ , and again assuming that there is no atmosphere, the quantity of light which the unit of surface would receive under these circumstances is represented by

$$\sin \vartheta.$$

Assuming, finally, that the atmosphere is present, the sun's light in passing through it will be weakened, and the unit of surface will therefore receive less light from the sun. If, for the sake of simplicity, it be assumed that the light of the sun is

\* Poggendorff's *Annalen*, vol. lxxii. p. 308.

homogeneous, the actual quantity of light which arrives, which may be designated by  $S$ , can be determined by the following equation,

$$S = \sin \vartheta \cdot e^{-\frac{a}{\sin \vartheta}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which  $e$  is the base of the natural logarithms,  $a$  the above-mentioned coefficient which depends on the degree of transparency of the atmosphere.

The difference,

$$\sin \vartheta - \sin \vartheta \cdot e^{-\frac{a}{\sin \vartheta}},$$

represents the loss which the direct solar light has experienced by the action of the atmosphere. Assuming now that this quantity of light is withdrawn from the direct solar light by the circumstance that it is reflected from any constituents of the atmosphere, it must (either directly or after experiencing several reflections in the atmosphere) partially reach the earth as diffused light, and partly be radiated into space. The question is, what fraction of this quantity of light reaches the earth? and in answering this question, the nature of the constituents of the atmosphere which effect the reflection must be taken into account. We will denote by  $Z$  this fraction, which varies with the position of the sun, and is therefore to be regarded as a function of  $\vartheta$ ; the quantity of light which falls upon the unit of surface as diffused light from the sky, and which may be designated by  $H$ , is determined by the equation

$$H = \sin \vartheta (1 - e^{-\frac{a}{\sin \vartheta}}) Z. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Dividing the equations (1) and (2), we obtain the desired ratio between the direct sunlight and the diffused light of the sky; that is,

$$\frac{S}{H} = \frac{e^{-\frac{a}{\sin \vartheta}}}{1 - e^{-\frac{a}{\sin \vartheta}}} \cdot \frac{1}{Z}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The magnitude  $Z$  depends mainly, as has already been stated, on the nature of the reflecting constituents. Such differences of the coefficient  $a$  as can occur in bright weather exert so small an influence on the magnitude  $Z$ , that in an approximate calculation this may be regarded as independent of  $a$ . Assuming that the reflection is occasioned by water-vesicles, the following values for  $Z$  are obtained from my previously published calculations:—

$\vartheta$	20°.	25°.	30°.	35°.	40°.	50°.	60°.
$Z$	0.575	0.606	0.632	0.654	0.673	0.701	0.721

These values we will here apply.

We will now compare the most complete of the above three series of observations, those made at Heidelberg, with the theoretical formulæ. For this purpose the coefficient  $a$  must be determined from one of the observed values of  $\frac{S}{H}$ . We will take the value which corresponds to the solar height  $40^\circ$ , because  $40^\circ$  is just the mean between  $20^\circ$  and  $60^\circ$ . This value is 1, and from this we get

$$a = 0.586.$$

Introducing this value for  $a$  into the equation (3), we can calculate  $\frac{S}{H}$  for other solar heights, and thus obtain the following values, which may be again collated with the observed values:—

Sun's altitude.	Calculated.	Experiments.
20°	0.38	0.35
25	0.55	0.48
30	0.71	0.65
35	0.86	0.82
40	1	1
50	1.24	1.37
60	1.43	1.60

If it be considered that in this calculation several cooperating circumstances have been disregarded, and that no perfect accuracy is to be ascribed to the observations, the agreement between the calculated and the observed values will be found to be sufficiently close. There is therefore no reason for saying that by these observations the hypothesis that the reflection is effected by the water-vesicles in the atmosphere is refuted.

I think, moreover, that comparisons of this kind are little fitted to decide on the accuracy or inaccuracy of the hypothesis; for the other cooperating circumstances, which can be but imperfectly taken into account in the calculation, have partly a far greater influence on the intensities of light than the nature of the reflecting constituents.

I remain, Gentlemen,

With great respect,

Yours,

R. CLAUDIUS.

Zurich, May 26, 1866.



VII. *On an Extension of the Principles of the Calculus of Variations.* By Professor CHALLIS, M.A., F.R.S., F.R.A.S.\*

THE considerations I am about to offer relative to the principles of the Calculus of Variations have arisen out of attempts to solve the problem of the maximum solid of revolution of given surface and given length of axis. That a solid exists, the largest of all solids of revolution whose surfaces are of given area and extend *continuously* from one extremity of the axis to the other, there can, I think, be no reason to doubt; and it will be a reproach to mathematical science if it remains undiscovered. I discussed this problem in the Philosophical Magazine for August 1861, and again in that for September 1862; and after full consideration of the reasoning there employed, I do not see how, according to the principles of the Calculus of Variations *as usually understood*, the line which by its revolution generates the surface of the required solid can be any other than the one which that reasoning gives, viz. a composite but continuous line consisting of equal ordinates at the extremities of the axis, connected by a portion of the curve generated by the focus of an hyperbola rolling on a straight line. But, as I have remarked at the beginning of another communication on the same problem in the Philosophical Magazine for March of this year, the solid enclosed by this surface does not possess the character of a maximum. The aforesaid reasoning can therefore only be regarded as a *reductio ad absurdum*, proving that the principles on which it rests require to be corrected or supplemented. This I consider that I have in effect done in the paper just cited; but as I find that the principles which the new method involves may be more distinctly stated, and the reasoning itself be put more logically than I have there succeeded in doing, I propose now to resume the subject.

The argument may commence with assuming the usual expression for the function  $u$  that is to be a maximum or minimum, viz.

$$u = B + \int (\delta y - p \delta x) A dx,$$

$B$  being the part extricated from the sign of integration, and containing the values of  $\delta x$  and  $\delta y$  at the limits, and  $A$  being a given function of  $x$ ,  $y$ , and the differential coefficients  $p$ ,  $q$ , &c. It may here be remarked that the substitution of  $x + \delta x$  and  $y + \delta y$  for  $x$  and  $y$  in the calculus of variations for the purpose of investigating rules for obtaining *functions* that satisfy the conditions of maxima and minima, is analogous to substituting in the differential calculus  $x + h$  and  $y + k$  for  $x$  and  $y$  in order

\* Communicated by the Author.

to obtain rules for finding maximum and minimum *values* of given functions. And as  $h$  and  $k$  are small indefinite quantities having no relation to each other, such also is the case with respect to  $\delta x$  and  $\delta y$ . The former substitution is supposed to change the form as well as the value of the function in which it is made; the latter only changes the value of the given function. This being understood, the maximum or minimum condition requires that the two parts of which  $u$  is composed should separately vanish. With respect to  $B$ , this is effected by the values of  $\delta y$  and  $\delta x$  at the limits of the integration, or given conditions to which those values are subjected. But since the other part contains the indeterminate and independent quantities  $\delta y$  and  $\delta x$ , it can vanish only by making the coefficients of these quantities vanish. Hence we have the two equations

$$A=0, \quad Ap=0.$$

These are differential equations the integration of which furnishes the function or functions by means of which the required maximum or minimum is calculated. I now make a remark which has an essential bearing on what follows. It has been usual to argue that because the second equation is satisfied if  $A=0$ , the two equations are always equivalent to each other, and that it suffices to take account of only one of them. This, however, as I am about to show, is a false conclusion; and to this error the difficulty of solving the before-named problem may be traced. The second differential equation is not of the same *degree* as the first; and it might happen that one is immediately integrable and not the other,—an analytical circumstance which of itself would make a distinction between them. To illustrate this point, let us first take an instance in which the two equations are equivalent, and then proceed with the discussion of the problem in hand, which will be found to be an instance of the contrary case.

Let it be required to find the line of given length which terminates at two given points, and encloses, with the straight line joining the points, a maximum area. By the usual process we obtain for this case

$$A dx = dx - d \cdot \frac{\lambda p}{\sqrt{1+p^2}}.$$

Hence

$$A p dx = dy - p d \cdot \frac{\lambda p}{\sqrt{1+p^2}} = dy - \frac{\lambda p dp}{\sqrt{1+p^2}}.$$

Here each of the equations  $A dx=0$  and  $A p dx=0$  is at once integrable; and each gives for the equation of the line,

$$(x+c)^2 + (y+c')^2 = \lambda^2.$$

Thus the second equation conveys the same information as the first; and as it is satisfied by  $\Lambda=0$ , there is no need in this instance to take it into consideration.

In the case of the other problem,

$$\delta \int (y^2 + \lambda \sqrt{1+p^2}) dx = 0,$$

$$\Lambda dx = 2y dx + \lambda dx \sqrt{1+p^2} - d \cdot \frac{\lambda y p}{\sqrt{1+p^2}} = 0,$$

$$\Lambda p dx = 2y p dx + \lambda p dx \sqrt{1+p^2} - p d \cdot \frac{\lambda y p}{\sqrt{1+p^2}} = 0,$$

or

$$\Lambda dy = 2y dy + \frac{\lambda dy}{\sqrt{1+p^2}} - \frac{\lambda y p dp}{(1+p^2)^{\frac{3}{2}}} = 0.$$

Hence the second equation is immediately integrable, giving

$$y^2 + \frac{\lambda y}{\sqrt{1+p^2}} = C.$$

But as the first equation is not in like manner integrable, this analytical circumstance indicates that the factor  $p$  is significant, and that we cannot, as in the former problem, dispense with the separate consideration of the equation  $\Lambda p = 0$ . It will therefore be proper to begin with inquiring what information this equation gives, before proceeding to the equation  $\Lambda = 0$ .

The expression for  $\Lambda$  being

$$2y + \frac{\lambda}{(1+p^2)^{\frac{1}{2}}} - \frac{\lambda y p}{(1+p^2)^{\frac{3}{2}}},$$

let us suppose that the required line is symmetrical with respect to the axis of  $x$ , or that for every positive value of  $y$  there is an equal negative value corresponding to the same abscissa. Then,

since  $(1+p^2)^{\frac{1}{2}}$  was put for  $\frac{ds}{dx}$ , which has opposite signs above and below the axis,  $s$  being always reckoned in the same direction along the curve, and since  $-\frac{q}{(1+p^2)^{\frac{3}{2}}}$  is the inverse of the

radius of curvature, which has the same sign for the positive as for the negative value of  $y$ , it follows that  $\Lambda$  changes sign with the change of sign of  $y$ . Hence, as the factor  $p$  changes sign in the same case,  $\Lambda p$  has the same sign on the opposite sides of the axis. Clearly also it has the same value. Consequently the integration of  $\Lambda dy = 0$  may be considered to embrace the two values of  $y$  corresponding to each value of  $x$ , and thus to satisfy the supposed condition of symmetry with respect to the axis of  $x$ .

Again, in the expression for  $A$  let us make  $y$  the independent variable instead of  $x$ ; so that, putting  $p'$  for  $\frac{dx}{dy}$  and  $q'$  for  $\frac{d^2x}{dy^2}$ , we have

$$A = 2y + \frac{\lambda p'}{(1+p'^2)^{\frac{1}{2}}} + \frac{\lambda y q'}{(1+p'^2)^{\frac{3}{2}}}.$$

Supposing now the line to be also symmetrical with respect to the axis of  $y$ , we shall have  $p'$  and  $\sqrt{1+p'^2}$ , or  $\frac{dx}{dy}$  and  $\frac{ds}{dy}$ , of different signs on the two sides of the axis, and the radius of curvature  $\frac{(1+p'^2)^{\frac{3}{2}}}{q'}$  of the same sign. Thus  $A dy$  neither changes sign nor magnitude by the change of sign of  $x$ . Consequently the integral of  $A dy = 0$  embraces the two values of  $x$  corresponding to each value of  $y$ , and thus satisfies the hypothesis of symmetry with regard to the axis of  $y$ .

But the integral of  $A dx = 0$  does not satisfy the supposition of symmetry with regard to the axis of  $x$ , because on that supposition  $A$  would change sign with the change of sign of  $y$ .

The above considerations enable us to draw a distinction between the equations  $A=0$  and  $Ap=0$ . If it were proposed to find, of all the surfaces of given extent generated by lines symmetrical with respect to the axis of  $x$  and also with respect to a perpendicular axis, that which encloses the greatest solid, the answer could not be given by the equation  $A=0$ , but might be given by  $Ap=0$ . In fact the solid deduced from the latter equation fulfils, as I am about to show, those conditions, and may therefore be regarded as the solution of a case of the general problem which involves the limitation of symmetry.

The differential equation  $Ap=0$  is satisfied if  $p=0$ ; and this mode of satisfying it is, by the rules of analysis, as much entitled to consideration as any other. By integration,  $y=c$ , which result, it will presently appear, is part of the answer to the problem. The same equation is satisfied by the integral obtained above, viz.

$$y^2 + \frac{\lambda y}{\sqrt{1+p^2}} = C,$$

the meaning of which is next to be considered. Since the straight line joining the two given points, designated hereafter as  $P$  and  $Q$ , coincides with the axis of  $x$ , and the required line has to pass through the points, that integral must be verified by  $y=0$ . Hence  $C=0$ . Consequently, taking account of the double sign of the radical, as the theory of equations demands,



we have the three equations

$$y=0, \quad y + \frac{\lambda}{\sqrt{1+p^2}}=0, \quad y - \frac{\lambda}{\sqrt{1+p^2}}=0.$$

I take occasion here to remark that, in my communication to the March Number (p. 220), I have not correctly indicated the signification of the factor  $y$ . Since, after putting  $C=0$ , the equation is satisfied by  $y=0$ , it is requisite to ascertain the meaning of this result. Considered by itself, it means that a straight line coincident with the axis of  $x$  is an answer in part to the proposed question. Now as the equation  $y=0$  is not inconsistent with the equation  $y=c$ , I have no reason to deny that that solution of the problem which is maintained by Mr. Todhunter in the June Number (p. 426) is one which the analysis includes. As, however, it gives a *broken* line—namely, a semi-circle having its diameter coincident with the axis, and its extremities connected with the points P and Q by straight lines—it does not supersede the inquiry on which I am engaged, which is, to find the *continuous* line that fulfils the condition of a maximum. Also, as the solution I refer to has sufficiently accounted for the equation  $y=0$ , we may, in prosecuting the other inquiry, omit this equation, and use instead of it  $y=c$ , joining with this equation the integrals of the two foregoing differential equations.

These equations give by integration

$$y^2 + (x + c')^2 = \lambda^2, \quad y^2 + (x + c'')^2 = \lambda^2;$$

so that we have at disposal three equations containing the three arbitrary constants  $c, c', c''$  for drawing a line from P to Q. It will, I suppose, be admitted that, consistently with the principles of the calculus of variations, the line may be *composite* in its character: what we have to ascertain is, whether the analysis indicates a *continuous* line—that is, one of which the component parts have a common tangent at each point of junction. Since two of the equations give equal circles having their centres at arbitrary positions on the axis of  $x$ , the line may evidently be drawn by making one of the circles pass through P, and the other, with its concavity turned in the opposite direction, through Q, and connecting them with the straight line parallel to the axis of  $x$  given by the third equation. But this would be no answer to the question unless the analysis indicated the mode of junction, and the positions of the points of junction, of the three lines. To ascertain whether it does so, recourse must be had to the part of the variation freed from the sign of integration. If the integral be taken from  $y=y_0$  to  $y=y_1$ , this part, by being

equated to zero, gives

$$\frac{\lambda p_1 y_1 \delta y_1}{\sqrt{1+p_1^2}} - \frac{\lambda p_0 y_0 \delta y_0}{\sqrt{1+p_0^2}} = 0;$$

and it is evident that this equation must apply to each circle separately. On applying it to the first circle, it will be seen that the second term vanishes, because, at the point P,  $y_0 \delta y_0 = 0$ , and

$\frac{p_0}{\sqrt{1+p_0^2}} = 1$ ,  $p_0$  being infinitely great; and that for the other

extremity of the arc, since  $y_1$  does not vanish and  $\delta y_1$  is indeterminate, we must have  $p_1 = 0$ . The same equation representing the integral from one extremity to the other of the second circular arc, the first term vanishes, because  $y_1 \delta y_1 = 0$ , and

$\frac{p_1}{\sqrt{1+p_1^2}} = 1$ , and the other because  $p_0 = 0$ ,  $y_0$  not vanishing,

and  $\delta y_0$  being indeterminate. We may hence infer, making the arbitrary constant  $c$  equal to  $\lambda$ , that the straight line and the arcs are continuous at the points of junction, and that each arc is a quadrant of a circle. According to this investigation the maximum solid has the form stated in my paper in the March Number, viz. a cylinder with hemispherical ends of the same radius. But it is not true, as there said, that a solid of this form is larger than any other solid of revolution having the same amount of surface and the same length of axis. I have given reasons above for concluding that the equation  $\Lambda p = 0$  gives a maximum, subject to the condition that the generating line of the surface, so far as regards the curved part, is symmetrical with respect both to the axis of revolution and to a perpendicular axis; and this condition the line we have found fulfils. The line which gives an absolute maximum can only be determined by means of the equation  $\Lambda = 0$ .

The foregoing reasoning sufficiently meets the objection adduced by Mr. Todhunter at the end of his communication in the June Number, namely, that the solution does not satisfy the equation  $\Lambda = 0$ . The answer is that it does not profess to satisfy this equation, but a different equation,  $\Lambda p = 0$ , for which reason it was necessary to take account of the factor  $p$  as well as the factor  $\Lambda$ . This having been done, the solution satisfies  $\Lambda = 0$  as far as regards the circular arcs, and  $p = 0$  as far as regards the straight line, and therefore satisfies the equation  $\Lambda p = 0$  through the whole extent. But I grant that as it does not satisfy  $\Lambda = 0$  through the whole extent, it does not give an absolute maximum. To obtain such a maximum it is necessary and sufficient that the integral be such as to satisfy  $\Lambda = 0$  throughout, because

this equation carries the other with it. I proceed now to the investigation of the line which gives the absolute maximum.

For this purpose we must use the integral of the equation  $\Lambda=0$ , or, changing for convenience the sign of  $\lambda$ , the equation

$$2ydx = \lambda dx \sqrt{1+p^2} - d \cdot \frac{\lambda yp}{\sqrt{1+p^2}}.$$

By integrating, we obtain the indefinite integral

$$2 \int y dx = \lambda s - \frac{\lambda y p}{\sqrt{1+p^2}} + C. \quad . \quad . \quad . \quad . \quad (\alpha)$$

It may now be assumed that the line has a limit in the direction of the axis of  $x$ , and that the abscissa of the extreme point is determined by making  $p$  infinite. Let  $y_0$  be the corresponding ordinate, and let  $s$  and the area  $\int y dx$  commence at that point. Then the arbitrary constant  $C$  is equal to  $\lambda y_0$ . The other limit of the integration may, if we please, be at the point for which  $s=s_1$  and  $p=0$ ; in which case we obtain the definite integral

$$2\int y'_0 dx = \lambda s_1 + \lambda y_0.$$

The supposition of a single value  $y_0$  of the ordinate at the limit for which  $p$  is infinite, implies that for other values of the abscissa there are *two* values of the ordinate. The above integration has been performed with reference to those values of the ordinate for which  $\frac{ds}{dx}$ , or  $\sqrt{1+p^2}$ , and  $p$  are positive, which set of values I have designated by the symbol  $y'$ . But when the integration has reference to the other set of ordinates, which I shall call  $y''$ ,  $\frac{ds}{dx}$  and  $p$  will change sign, while  $\frac{p}{\sqrt{1+p^2}}$  will retain the same sign. Hence the integral taken from  $s=0$  to  $s=-s_2$ , and from  $p=\infty$  to  $p=0$ , gives a second definite integral, viz.

$$2\int y'' dx = -\lambda s_2 + \lambda y_0.$$

By subtracting this from the other, the result is

$$\int (y' - y'') dx = \frac{\lambda}{2} (s_1 + s_2).$$

Now it is evident that this equation is satisfied by the supposition that the line is a *circle*. For in that case, since  $p=0$  for the extreme ordinates, the area is a semicircle,  $s_1+s_2$  is the length of the semicircular arc, and  $\lambda$  is the radius of the circle. If the integrations be taken from the ordinate  $y_0$  to *any* ordinates  $y_1$

and  $y_2$  having a common abscissa, the expression for the segmental area  $\int (y' - y'') dx$  will be

$$\frac{\lambda}{2} (s_1 + s_2) - \frac{\lambda}{2} \left( \frac{y_1 p_1}{\sqrt{1 + p_1^2}} - \frac{y_2 p_2}{\sqrt{1 + p_2^2}} \right),$$

$p_1$  and  $p_2$  being the values of  $p$  for the ordinates  $y_1$  and  $y_2$ . In the March Number I have shown by simple geometrical reasoning, which need not be repeated here, that, on the supposition that the line is a circle, this expression gives the area of the circular segment cut off by the difference of the limiting ordinates. Hence it may be inferred that the form of the curve which satisfies the condition of a maximum can be no other than that of the circle, and that the position of its centre is at disposal for fulfilling required conditions.

I find that Mr. Todhunter, in the communication before referred to, has objected to this solution also that it does not satisfy the equation  $\Lambda = 0$ . This objection has apparently been made without taking into consideration that the function  $\Lambda$ , because it contains a radical, has *two* values, and that the principles of analysis demand that both should be taken into account.

Since the radical has arisen from substituting  $\sqrt{1 + p^2}$  for  $\frac{ds}{dx}$ , it implies that there are two ordinates to the same abscissa, and that the two sets of ordinates belong to parts of the curve which have their convexities turned opposite ways relatively to the axis of  $x$ . In that case  $\frac{p}{\sqrt{1 + p^2}}$  has the same sign for both sets.

Hence, using dashes to distinguish between them, we have the two equations

$$2y'dx = \lambda ds' - d \cdot \frac{\lambda y' p'}{\sqrt{1 + p'^2}},$$

$$2y''dx = -\lambda ds'' - d \cdot \frac{\lambda y'' p''}{\sqrt{1 + p''^2}};$$

and by subtraction,

$$(y' - y'')dx = \frac{\lambda}{2} (ds' + ds'') - \frac{\lambda}{2} \left( d \cdot \frac{y' p'}{\sqrt{1 + p'^2}} - d \cdot \frac{y'' p''}{\sqrt{1 + p''^2}} \right).$$

This last equation, inasmuch as it takes account of both values of  $\Lambda$ , is the one which the form of the curve is required to satisfy. To draw any inference from one value of  $\Lambda$  and exclude the other would be nothing short of error. By integrating, and determining the arbitrary constant so that the area  $\int (y' - y'') dx$ , and the arcs  $s'$  and  $s''$  commence where  $p' = p'' = \infty$ , and  $y' = y'' = y_0$ ,



the same equation is obtained as that which, it has already been shown, indicates that the curve is a circle. In the case of the function  $Ap$ , there were not two equations corresponding to two sets of values, because by the condition of symmetry the two ordinates to the same abscissa were equal with opposite signs, and the same form of the function consequently included both sets of values.

When I made the communication contained in the March Number, I had not recognized the distinction which I have now drawn between the conditional and the absolute maximum, and in consequence supposed the first part of the solution to apply to the case in which the given surface  $h^2$  is less than  $4\pi c^2$ , the surface of the sphere whose diameter  $=PQ$ , and the latter part to apply when  $h^2$  is greater than  $4\pi c^2$ . But the present reasoning has shown that the determination of the absolute maximum is not subject to restriction, and that the line which generates the surface of the maximum solid is a segment of a circle of which the line joining the given points is the chord, whether  $h^2$  be greater or less than  $4\pi c^2$ . The other conclusions arrived at in the former paper, especially the interesting one respecting the form of the maximum ring of given superficies, I have not seen reason to retract or modify.

It has already been stated in the March Number that the maximum solid obtained in the first part of this investigation, namely, the cylinder with hemispherical ends, is found by analytical calculation to be greater than a solid of the form of a prolate spheroid, whether the eccentricity be very small or nearly equal to unity. I have since ascertained that it is also greater than the solid which has for the generating line of its surface a circular arc connected with the given points by two tangents at its extremities of equal length. If, however, the generating line be a circular arc at right angles to the axis at one of the given points, and connected with the other by a tangent at its extremity, the solid will be found to be greater than the cylindrical one. For, in fact, this line, though continuous, does not, like the preceding one, satisfy the condition of symmetry with respect to a perpendicular axis. Moreover, I have ascertained that this unsymmetrical solid is less than that the generating line of whose surface is the segment of a circle passing through the given points; which, according to the foregoing solution, is the absolute maximum of the solids of continuous form.

It may be further remarked that as a sphere is the greatest solid of given superficies, there may be all sorts of solids of revolution of *discontinuous* form intermediate in magnitude between the sphere and the solid which I call the absolute maximum. For instance, let the generating line be a semicircle connected

at its extremities with the given points by two straight lines inclined at small angles to the axis PQ. It is evident that by varying the angles of inclination, solids of different degrees of magnitude will be obtained, and so much the greater as those angles are less, the maximum of all being that for which the angles of inclination are indefinitely small. This maximum is the same as that which results when the equation  $y=0$  is taken into account, which Mr. Todhunter regards as the only solution which our problem admits of. It satisfies the equation  $Ap=0$ ; but not the equation  $A=0$ . I assent to the opinion expressed by M. Lindelöf (*Leçons de Calcul des Variations*, p. 225), that this is not properly a solution of the proposed problem. I cannot perceive that it differs essentially from the solution of the unconditioned problem of the maximum solid of given surface; and, at least, it does not possess the same interest as the determination of the form of the maximum solid which has a continuous surface passing through the given points.

If I have at length succeeded in effecting a solution of this perplexing problem, I have at the same time pointed out the reasons of the failure of previous attempts. One reason appears to have been an imperfect knowledge of the rules of application of the integrals of differential equations whose degree is higher than the first. Instances of such application have been rarely handled by analysts, and the principle of discontinuity which they generally involve is hardly yet fully admitted. As far as I am aware, the first case of an integral of this class in the calculus of variations leading to a discontinuous solution is that which occurs in the solution of the problem of the shortest course of a ship, which is given in the September Number of 1862 (p. 197), but was originally published so long since as 1834 in vol. i. of the *Philosophical Magazine* for that year (p. 33). But the chief cause of failure, which, however, is connected with the other, was the confounding of two differential equations,  $A=0$  and  $Ap=0$ , of different degrees, and regarding them as identical. On the general principles of analysis it might be argued that, while there are cases in which the equations lead to identical results, the very fact of there being two equations is evidence that there are also cases in which the results are not identical. For no symbolical difference can be entirely without meaning. The foregoing investigation has, I think, shown that in the present instance one equation points to a relative or conditional maximum, and the other to an absolute maximum. As I am not aware that the two equations have been similarly treated in any previous researches, I have ventured to call the use I have made of them *an extension of the principles of the Calculus of Variations*.

Cambridge, June 16, 1866.

VIII. *Food in its relations to various exigencies of the Animal Body.* By J. B. LAWES, F.R.S., F.C.S., and J. H. GILBERT, Ph.D., F.R.S., F.C.S.\*

THE appearance in the June (Supplementary) Number of the Philosophical Magazine of the interesting paper by Professors Fick and Wislicenus "On the Origin of Muscular Power," and the further interest excited in the subject by Professor Frankland's recent lecture at the Royal Institution, seem to render it opportune that the important question of the connexion between certain constituents of food and certain exigencies of the animal body should receive a little further consideration at the present time. Professor Frankland truly said that, since the appearance of Baron Liebig's masterly and highly suggestive work 'On Organic Chemistry in its applications to Physiology and Pathology' in 1842, his views of the relation of the nitrogenous and the non-nitrogenous constituents of food to certain requirements of the animal organism have been pretty generally adopted by text-book writers. It is also true that authorities on the subject of the chemistry of food have, even so recently as last year and this, either directly maintained or taken for granted the correctness of Baron Liebig's views. It is, however, not the case, as was also assumed by Professor Frankland, that those views have remained unquestioned excepting in the one or two instances of criticism to which he referred.

This question, in various aspects, has occupied a great deal of our own attention for many years past; and so long ago as 1852 we advocated substantially the views now adopted by Professors Fick, Wislicenus, and Frankland; and we have on various occasions since that date expressed them with greater definiteness, and urged them the more emphatically, as new experimental evidence either of others or ourselves seemed to lend them support or confirmation. It may be well, therefore, to state very briefly the course of our own investigations bearing upon the subject, and also the conclusions that we have based upon them.

In Baron Liebig's work above alluded to, and also in subsequent publications, he treated of the food requirements of the animal body generally—that is, under different conditions; and starting from the fundamental assumptions, on the one hand, of the direct connexion of the nitrogenous or, as he designated them, the "*plastic*" constituents of food, not only with the formation in the animal body of the compounds containing nitrogen, but also with the development of muscular power, and, on the other, of the general relationship of the non-nitrogenous constituents of food with respiration, the development of heat, and

\* Communicated by the Authors.



the deposition of animal fat, he concluded that the relative value of different foods, as such, was to a great extent dependent on, and even measurable by, the proportion of nitrogenous constituents which they contained.

It was upon the assumption of the broad and fundamental classification of the constituents of food according to their various offices in the animal economy, as above stated, that numerous analyses of food were undertaken, and, founded upon the results obtained, Tables constructed professing to arrange current articles of food, both of man and other animals, according to their comparative values as such; and whether the object were the feeding of animals for the production of milk, the so-called fattening of them for the production of meat, or the support of the body for the exercise of muscular power, the proportion of nitrogenous constituents was generally taken as the measure of that value.

Omitting, for the sake of brevity, any special reference to the labours or views of others, it will suffice here to make a few such quotations from Baron Liebig's works as will best convey shortly in his own words a pretty clear indication of his own views, and at the same time pretty fairly represent those of a large proportion both of systematic writers and experimenters, on the points in question. Speaking of the nitrogenous constituents of food, he said:—

“It is found that animals require for their support less of any vegetable food in proportion as it is richer in these peculiar matters, and cannot be nourished by vegetables in which these matters are absent.” (Chemical Letters, 3rd edition, p. 349.)

Again:—

“The admirable experiments of Boussingault prove, that the increase in the weight of the body in the fattening or feeding of stock (just as is the case with the supply of milk obtained from milch cows), is in proportion to the amount of plastic constituents in the daily supply of fodder.” (Chemical Letters, 3rd edit. p. 369).

In regard to the exercise of force, he said:—

“As an immediate effect of the manifestation of mechanical force, we see, that a part of the muscular substance loses its vital properties, its character of life; that this portion separates from the living part, and loses its capacity of growth and its power of resistance. We find that this change of properties is accompanied by the entrance of a foreign body (oxygen) into the composition of the muscular fibre (just as the acid lost its chemical character by combining with zinc); and all experience proves, that this conversion of living muscular fibre into compounds destitute of vitality is accelerated or retarded according to the amount of force employed to produce motion. Nay, it may safely be affirmed, that they are mutually proportional; that a rapid transformation



of muscular fibre, or, as it may be called, a rapid change of matter, determines a greater amount of mechanical force; and conversely, that a greater amount of mechanical motion (of mechanical force expended in motion) determines a more rapid change of matter." (Organic Chemistry in its applications to Physiology and Pathology, 1842, pp. 220 & 221.)

And again:—

"The amount of azotized food necessary to restore the equilibrium between waste and supply is directly proportional to the amount of tissues metamorphosed.

"The amount of living matter, which in the body loses the condition of life, is, in equal temperatures, directly proportional to the mechanical effects produced in a given time.

"The amount of tissue metamorphosed in a given time may be measured by the quantity of nitrogen in the urine.

"The sum of the mechanical effects produced in two individuals, in the same temperature, is proportional to the amount of nitrogen in their urine; whether the mechanical force has been employed in voluntary or involuntary motions, whether it has been consumed by the limbs or by the heart and other viscera." (Ibid. p. 245.)

Our own direct experiments have had reference chiefly to the feeding of fattening animals; but the characteristic food requirements of the body, when fed with the view to the exercise of muscular power, have also been made the subjects of inquiry.

Referring to the feeding of fattening animals, the question arises, whether in the use of the currently adopted food-stuffs *the amount of food consumed by a given weight of animal within a given time*, and *the amount of increase produced* are more influenced by the amount of the nitrogenous or of the non-nitrogenous constituents which the food supplies; that is to say, whether the sum of the requirements of the animal system under these circumstances is such that, in the use of the ordinary articles of food, the *amount taken* or *increase produced* will be more regulated, or measurable, by the supplies of the nitrogenous or "flesh-forming" constituents, or by those of the more specially respiratory and fat-forming non-nitrogenous constituents.

To acquire the data necessary for the satisfactory solution of this question, some hundreds of animals—oxen, sheep, and pigs—have been experimented upon. Comparative lots being selected, the general plan of the feeding-experiments was to give to some a fixed and limited amount of food of known composition in regard to its contents of nitrogenous and non-nitrogenous constituents, to others a fixed and limited amount of food of different composition in this respect, and to allow all to take as much as they chose to eat of some other food, also of known compo-

sition, the quantity consumed being weighed. In some cases a single description of food only, or a mixture of several descriptions in known proportions, was given *ad libitum*, but weighed; and in others, several descriptions of food were allowed, each separately, *ad libitum*, but weighed. It will be seen that in this way great variation in the amount and proportion of the nitrogenous and non-nitrogenous constituents supplied was attained, whilst the animals, according to the nature of the food within their reach, fixed for themselves the limit of their consumption. All such comparative experiments were conducted for many weeks, or even for several months, consecutively, and the weights of the animals themselves were determined at the commencement, at stated periods during the progress, and at the conclusion of the experiment\*.

To determine the character and composition of the gross increase in live-weight, the weights of the individual internal organs and of other separated parts of several hundred animals of different descriptions and in different conditions as to age, maturity, and fatness were taken; whilst in some carefully-selected cases the total amounts of fat, nitrogenous substance, mineral matter, and water were determined†.

It is obvious that in the case of fattening animals, the amount of food consumed *in relation to a given body-weight within a given time* will be regulated, not only by the demands of the system for the support of respiration, perspiration, &c., and for the repair of normal waste of nitrogenous substance, but also by the additional requirements for growth and increase; whilst, on the other hand, the amount required to be consumed *for the production of a given amount of increase* will, in its turn, include that due to the demands of the system for respirable and perspirable matter and the repair of the waste of nitrogenous substance. Whether, however, the experimental results were calculated so as to show the amount consumed per 100 lbs. live-weight per week, or to

\* "On the Composition of Foods in relation to Respiration and the Feeding of Animals." Report of the British Association for the Advancement of Science for 1852. "Agricultural Chemistry: Sheep-feeding and Manure," part 1, Journ. Roy. Ag. Soc. Eng. vol. x. part 1, 1849. "Reports of Experiments on the Comparative Fattening Qualities of different Breeds of Sheep," *ibid.* vol. xii. part 2, 1851; vol. xiii. part 1, 1852; vol. xvi. part 1, 1855. "Agricultural Chemistry: Pig Feeding," *ibid.* vol. xiv. part. 2, 1853. "On the Equivalency of Starch and Sugar in Food," Rep. Brit. Assoc. for 1854.

† "Experimental Inquiry into the Composition of some of the Animals Fed and Slaughtered as Human Food," Phil. Trans. part 2, 1859; also Proceedings of the Royal Society, vol. ix. p. 348. "On the Composition of Oxen, Sheep, and Pigs, and of their Increase whilst Fattening," Journ. Roy. Ag. Soc. Eng. vol. xxi. part 2, 1860. "On the Chemistry of the Feeding of Animals for the production of Meat and Manure," Proc. Roy. Dub. Soc. March 31, 1864.

produce 100 lbs. increase in live-weight, it was strikingly brought out in all comparable experiments that it was in neither case the amount of nitrogenous constituents, but in both the amount of digestible or available non-nitrogenous constituents (or total organic substance) of the food that had regulated the result obtained.

Referring the reader to our former papers for all experimental details, and for the fuller discussion of the results and statement of our conclusions, we will close this part of the subject in words quoted from a paper given at the Meeting of the British Association at Belfast in 1852\*. The sentence as quoted had reference to the results obtained with sheep; but subsequently those obtained with pigs were summarized in almost the same words:—

“ . . . if we consider that it is the results obtained under the subtle agency of animal life that we are seeking to measure and express in figures, and if we also bear in mind the various sources of modification to which our actual figures must be submitted in order to attain their true indications, we think that it cannot be doubted that, beyond a limit below which few, if any, of our current fattening food-stuffs are found to go, it is their available non-nitrogenous constituents, rather than their richness in the nitrogenous ones, that measure both the amount consumed to a given weight of animal, within a given time, and the increase in weight obtained.”

Bearing in mind the nature of the respiratory process, and the great influence which its demands must necessarily exercise over the amount of food consumed, it will scarcely appear surprising that *consumption* at least should be chiefly regulated by the supply in the food of non-nitrogenous constituents; but that *the amount of increase* obtained in feeding animals for the butcher should also bear a closer relationship to the supply of the non-nitrogenous than to that of the nitrogenous constituents, might perhaps well be looked upon as inconsistent with the currently adopted views as to the highly nitrogenous character of the increase of animals fed for human food, and, indeed, of the highly nitrogenous character of the animal portion of human food generally.

The investigation into the composition of the fattening animals, and their increase, above alluded to, showed, however, how small was the proportion of the nitrogenous substance of the food that was stored up in the increase of the animal, and also that the proportion of fat in the increase was much greater than had previously been supposed. The results further led to the remarkable conclusion, that, reckoning the fat

\* “On the Composition of Foods in relation to Respiration and the Feeding of Animals,” Report of the British Association for the Advancement of Science for 1852.



of the estimated total consumed portions of animals admitted to be in only a proper condition of fatness into its starch equivalent, there was, on the average, a higher proportion of so-reckoned non-nitrogenous substance to one of nitrogenous substance in such animal food than in bread itself. It was concluded, indeed, that, on the large scale, the introduction of animal aliments into our otherwise chiefly farinaceous diet did not increase, but diminish the *relation* of the nitrogenous or so-called "flesh-forming," to the non-nitrogenous constituents (reckoned according to their respiratory and fat-forming capacity) in the collective food. The important bearing of these facts in forming an estimate of the characteristics of different human dietaries will be at once apparent.

So much, then, for the characteristic food requirements of animals exposed to as little exertion as possible, and fed with the express view of accumulating flesh and fat in their bodies. Concurrently with the earlier experiments to determine the relations of food and body-weight and increase above referred to, the question of the relation of the amount of the constituents voided (especially the nitrogen) in the liquid and solid excrements to that in the food consumed, was also investigated. Consistently with the results obtained in regard to the amount and character of the increase resulting from the consumption of very different amounts of nitrogenous substance, it was found that the amount of nitrogen voided by fattening animals fed under equal conditions as to the exercise of force, bore a very direct relation to that supplied in the food. So direct, indeed, is the connexion between the composition of the matters excreted and that of the food consumed, that we have constructed Tables showing the relative value of the manure produced by fattening animals from a given weight of different food-stuffs according to the composition of the latter.

But more to our present purpose—so striking were the results obtained in regard to the connexion between the composition of the food on the one hand, and the amount consumed, the amount and character of the increase produced, and the composition of the excreted matters, on the other, and, on some important points, so contrary in their indications to the prevailing views, that we were led at once to turn our attention to human dietaries, and especially to a consideration of the management of the animal body undergoing somewhat excessive labour, as, for instance, the hunting horse, the racer, the cab-horse, and the fox-hound, and also pugilists and runners. The conclusions to which we were led by this study were briefly summarized in 1852 as follows\* :—

\* Report of the British Association for the Advancement of Science for 1852.



" . . . . . that in the cases, at least of ordinary exercise of force, the exigencies of the respiratory system keep pace more nearly with the demand for nitrogenous constituents of food than is usually supposed."

And further:—

"A somewhat concentrated supply of nitrogen does, however, in some cases, seem to be required when the system is over-taxed—as for instance, when day by day more labour is demanded of the animal body than it is competent without deterioration to keep up; and perhaps also, in the human body, when under excitement or excessive mental exercise. It must be remembered, however, that it is in butchers' meat, to which is attributed such high flesh-forming capacity, that we have also, in the fat which it contains, a large proportion of respiratory material of the most concentrated kind. It is found, too, that of the dry substance of the *egg*, 40 per cent. is pure fat.

"A consideration of the habits of those of the labouring classes who are under- rather than over-fed, will show, that they first have recourse to fat meat, such as pork, rather than to those which are leaner and more nitrogenous—thus perhaps indicating, that the first instinctive call is for an increase of the respiratory constituents of food. It cannot be doubted, however, that the higher classes do consume a larger proportion of the leaner meats; though it is probable, as we have said, that even with these, as well as pork, more *fat*, possessing a higher respiratory capacity than any other constituent of food, is taken into the system than is generally imagined. Fat and butter, indeed, may be said to have about twice and a half the respiratory capacity of starch, sugar, &c. It should be remembered, too, that the classes which consume most of the leaner meats, are also those which consume the most butter, sugar, and in many cases, alcoholic drinks also.

"It is further worthy of remark, that wherever labour is expended in the manufacture of staple articles of food, it has generally for its object the concentration of the *non-nitrogenous*, or more peculiarly respiratory constituents. Sugar, butter, and alcoholic drinks are notable instances of this. Cheese, which at first sight might appear an exception, is in reality not so; for those cheeses which bring the highest price are always those which contain the most butter; whilst butter itself is always dearer than cheese.

"In conclusion, it must by no means be understood that we would in any way depreciate the value of even a somewhat liberal amount of nitrogen in food. We believe, however, that on the current views too high a relative importance is attached to it; and that it would conduce to further progress in

this most important field of inquiry if the prevailing opinions on the subject were somewhat modified\*.”

It will be borne in mind that at the time the statement of view here quoted was made, the opinions expressed were directly contrary to all recognized authority on the subject, and it is since that date that so much evidence has been accumulated in regard to the amounts of urea, and the amounts of carbonic acid and other products, given off under varied conditions as to food and exercise. Still, from the facts even then at command, it was concluded that the increased demand for food resulting from the exercise of muscular power was specially characterized by the requirement for an enhanced amount of the non-nitrogenous constituents. Confirmatory evidence was, however, not long wanting.

In 1854 we selected two pigs as nearly as possible of equal weight and character; to one was given, *ad libitum*, lentil-meal (containing about 4 per cent. of nitrogen), and to the other, also *ad libitum*, barley-meal (containing less than 2 per cent.). After the animals had been kept for a certain time on their respective foods, one comparative experiment was conducted for a period of three days, and another for a period of ten days. The weights of the animals were taken at the beginning and at the end of each experiment, and, besides other particulars, the amounts of nitrogen consumed in food, and voided as urea, were determined†. The result was, that with exactly equal conditions as to exercise, both animals being in fact at rest, the amount of urea passed by the one feeding on the highly nitrogenous lentil-meal was more than twice as great as that passed by the one fed on the barley-meal. We have since made other such experiments with similar results.

It was clear, therefore, that the rule laid down by Liebig, and assumed to be substantially correct by so many writers, did not hold good—namely, that “The sum of the mechanical effects produced in two individuals, in the same temperature, is proportional to the amount of nitrogen in their urine, whether the mechanical force has been employed in voluntary or involuntary motions, whether it has been consumed by the limbs or by the heart and other viscera”—unless, indeed, as has been assumed by some experimenters, there is, with increased nitrogen in the food, an increased amount of mechanical force employed in the

\* It is worthy of remark, too, that neither are the most highly nitrogenous wheats the most valued by the baker for the purpose of bread-making, nor is the most highly nitrogenous bread the most valued by the chiefly bread-fed working man. See “On some Points in the Composition of Wheat-grain, its Products in the Mill, and Bread,” Journ. Chem. Soc. vol. x. 1858.

† Phil. Trans. part 2, 1859, p. 554.

“involuntary motions” sufficient to account for the increased amount of urea voided.

It was at any rate obvious that, if the amount of urea voided by one animal at rest could be from two to three times as great as that voided by a similar animal also at rest, and under otherwise equal conditions, provided only that the food of the one contained from two to three times as much nitrogen as that of the other, the amount of urea passed could not be any measure of the amount of muscular power exerted; and this evidence, considered in connexion with that relating to the demands of the system not only of the fattening animal but of the animal body fed with a view to mechanical exertion, afforded further confirmation of the view we had already put forward as above quoted, and also led to the extension and more definite expression of it.

The results of Bischoff and Voit, conducted through a period of many months, with a dog, either submitted to hunger or fed from time to time on foods containing very different amounts of nitrogenous substance, showed a very variable amount of urea voided, although the animal were kept under equal conditions as to exercise. Still, on the publication of those results in 1860, the authors assumed that although there had been no greater exercise of force manifested in the form of external work, yet when the amount of nitrogenous substance in the food was greater, and the amount of urea voided correspondingly greater, there must have been a corresponding increase in the force exercised in the conduct of the actions proceeding within the body itself in connexion with the disposition of the increased amount of nitrogenous substance consumed. When, however, they subsequently found that the amount of urea passed by the animal when subjected to somewhat severe labour was, other things being equal, no greater than when at rest, whilst the carbonic acid evolved was much increased by such exercise, their view was of necessity somewhat modified.

Again, the results of Dr. Edward Smith, which showed great variation in the amount of urea passed when there was concurrent variation in the amount of nitrogenous substance in the food, and comparatively little variation in the amount of urea voided with great variation in the amount of labour performed, but, on the other hand, great increase in the carbonic acid evolved with increased exercise of force, obviously still further pointed to the correctness of the view that with muscular exertion there was a more marked increased demand for the non-nitrogenous than for the nitrogenous constituents of food.

That this was the necessary conclusion from the results of our own investigations, and also from those of the researches of Bidder and Schmidt, Bischoff, Voit, Pettenkofer, E. Smith, and others, we have frequently maintained. Indeed the view urged



in public discussion has been, that all the evidence at command tended to show that by an increased exercise of muscular power there was, with increased requirement for respirable material, probably no increased production and avoidance of urea, unless, owing to excess of nitrogenous matter in the food, or a deficiency of available non-nitrogenous substance, or diseased action, the nitrogenous constituents of the fluids or solids of the body were drawn upon in an abnormal degree for the supply of respirable material.

From the facts briefly summarized in the foregoing pages, it will be obvious that the generally accepted views in regard to the adaptation of food, according to its composition, to the various exigencies of the animal body, require modification in other respects than in so far as they relate to the source or development of muscular power alone. At the same time we hail with much satisfaction the confirmation of the views we have so long maintained on the point (in opposition to general authority) which has recently been afforded by the results of the interesting, though limited experiment of Professors Fick and Wislicenus, so ably discussed by them in their paper, and by Professor Frankland in his lecture.

#### IX. *On the Action of Aqueous Vapour on Terrestrial Radiation.*

By Lieut.-Colonel STRACHEY, F.R.S.\*

THE soundness of Dr. Tyndall's conclusions as to the effect of watery vapour in the air on the passage of radiant heat, has, I understand, been disputed by some high authorities. The testing of these conclusions by observations made with no reference to the question at issue, will therefore probably be interesting to persons who have followed Dr. Tyndall's admirable and, as it seems to me, altogether satisfactory researches. Something of the sort has already been undertaken, and the results have been published in the *Philosophical Magazine*. My own method of examination is somewhat different from that to which I thus refer, and seems, in some respects at least, preferable. The views which I shall now briefly state were, I may add, adopted some little time back, in the course of an investigation on another meteorological problem.

In examining the character of the diurnal variation of the barometrical pressure as recorded in the Madras Observations, and in considering the probable connexion between the variations of pressure and those of temperature, it became apparent to me that the principal cause of the increased or diminished range of air-temperature was to be found in the greater or less degree of clearness of the sky in the various months of the year. Following up this idea, I further saw that the degree of cloudiness of the sky was greatly dependent on the quantity of vapour in

\* Communicated by the Author.



the air. It then occurred to me to ascertain whether the quantity of vapour appeared to influence the variation of diurnal temperature, irrespective of the action of clouds. For this purpose I selected from the observations those days on which the sky was almost free from clouds, and noted the march of the thermometer.

The varying power of the sun in its annual course from north to south prevents any immediate comparison of the gain of heat during the day being available to test the influence of the watery vapour in absorbing the sun's heat. But the loss of heat at night being essentially dependent on the radiation from the earth into space through the air, a reliable standard was here to be got. I accordingly calculated the fall of temperature from 6<sup>h</sup> 40<sup>m</sup> P.M., Madras time, to 5<sup>h</sup> 40<sup>m</sup> A.M. next morning for the days selected as sufficiently clear; at the same time the mean tension of vapour during the night was also calculated, and the temperature at 6<sup>h</sup> 40<sup>m</sup> P.M. noted. The results, arranged according to the quantity of vapour, for the years 1841, 1842, 1843, and 1844 are given in the annexed Table:—

1844.				1844 (continued).			
Tension of vapour.	Fall of thermometer, 6h 40m to 17h 40m.	Thermometer at 6h 40m.	Percentage of clear sky.	Tension of vapour.	Fall of thermometer, 6h 40m to 17h 40m.	Thermometer at 6h 40m.	Percentage of clear sky.
inch.				inch.			
1.00	2.7	87.2	.98	.71	7.2	81.2	.92
.97	3.6	87.4	.92	.71	8.5	82.0	1.00
.95	4.6	86.4	.91	.71	7.6	81.3	.92
.94	4.8	86.4	.98	.71	5.4	79.0	.99
.94	4.5	86.1	.96	.69	5.5	77.8	.96
.94	4.8	85.8	.90	.69	7.7	81.2	1.00
.93	4.5	86.5	1.00	.68	6.3	77.7	.97
.92	5.0	86.3	.99	.67	7.6	77.7	1.00
.92	6.1	87.0	.96	.67	7.5	77.7	.91
.92	4.2	86.3	.96	.67	11.2	81.8	1.00
.91	5.0	85.5	.95	.67	7.6	79.0	.91
.91	4.7	86.5	.97	.67	7.3	79.4	.98
.91	5.2	85.7	.94	.65	9.5	78.0	1.00
.90	5.2	86.7	.95	.65	8.6	78.4	.94
.90	3.4	86.1	.97	.64	8.6	77.0	.96
.89	5.3	86.3	.98	.64	7.5	77.2	.96
.86	6.2	84.6	.90	.63	9.5	80.5	1.00
.81	5.7	83.5	.93	.63	7.6	77.3	.95
.81	6.8	84.0	.94	.62	9.1	77.2	1.00
.80	5.0	83.3	.91	.62	6.9	77.8	1.00
.77	7.1	83.2	1.00	.61	9.6	77.6	1.00
.76	6.6	82.1	.97	.60	9.6	78.0	1.00
.75	5.8	80.2	.99	.59	12.2	79.9	1.00
.74	7.5	81.8	.94	.59	8.1	75.1	1.00
.74	6.7	81.8	.98	.58	7.0	76.0	.95
.74	9.9	83.7	.04	.58	9.4	77.2	1.00
.74	5.9	80.0	.90	.58	8.4	79.3	.90
.73	6.7	82.2	.97	.57	9.1	75.5	.99
.72	5.5	79.3	.98				

TABLE (continued).

1843.				1842 (continued).			
Tension of vapour.	Fall of thermometer, 6h 40m to 17h 40m.	Thermometer at 6h 40m.	Percentage of clear sky.	Tension of vapour.	Fall of thermometer, 6h 40m to 17h 40m.	Thermometer at 6h 40m.	Percentage of clear sky.
inch.				inch.			
·93	4·4	85·2	·98	·70	7·5	78·3	1·00
·93	5·0	85·2	·95	·69	8·2	78·9	·99
·92	5·3	85·8	·91	·69	9·1	80·3	·99
·90	6·2	85·1	·98	·69	9·5	80·3	·95
·88	4·2	84·9	·93	·65	10·6	81·2	1·00
·85	6·7	85·5	·96	·65	12·0	81·7	·99
·81	5·7	83·0	·96	·64	9·4	78·7	1·00
·75	6·4	81·6	·93	·61	11·6	79·3	·98
·72	5·7	77·5	·96	·57	9·3	77·3	·97
·71	5·2	80·2	·94	1841.			
·70	7·1	81·0	·98				
·70	7·3	79·8	·97	·97	5·4	84·0	·91
·69	6·6	76·9	1·00	·93	4·5	84·0	·98
·68	7·5	77·8	·96	·91	5·8	84·5	·91
·67	8·2	78·6	1·00	·91	4·9	84·1	·93
1842.				·88	8·5	87·0	·91
				·86	6·3	84·7	·93
·96	5·0	85·5	·92	·83	6·7	82·7	·92
·95	4·9	84·2	1·00	·71	5·5	77·8	·99
·94	5·6	85·9	·96	·70	10·8	84·7	·98
·93	5·8	86·6	·98	·66	6·8	76·5	·99
·89	6·5	85·4	1·00	·64	6·0	75·4	·97
·89	6·2	85·2	·99	·64	7·0	76·5	·98
·71	8·7	79·1	1·00	·63	6·7	76·2	·97
·71	8·2	78·8	1·00	·58	6·5	74·8	1·00

The general conclusion that the loss of heat by radiation from the earth at night is directly affected in a very considerable degree by the quantity of vapour in the air, seems to be unmistakeably indicated by these figures. It is necessary to be prepared for considerable discrepancies in single observations; for though it is no doubt true that the loss of heat at night on the earth generally is essentially due to radiation into space, yet this will not be exactly the case at any particular place. The air, the temperature of which was measured and noted in the Madras observations, was of course in motion, and probably, or rather certainly, had acquired its temperature as it came up from some distant place to Madras. The observed fall of temperature, therefore, has reference to the average condition of the earth, and of the sky over it, throughout the region traversed by the current. There will have been variations of the heat of the earth's surface, of the serenity of the sky, and of the quantity of vapour in sus-

pension over the whole area traversed by the current of air; and such variations will of course have affected the final results noted. Further, the means of determining the clearness of the sky are very imperfect, and important differences of transparency may occur of which it is impossible to judge by the eye alone, the register of the state of the sky being a mere eye estimate.

I have thought that the records for the four years, which I have taken at random, will be sufficient to explain the method adopted, and to show the character of the support given in this way to Dr. Tyndall's views. I may add, however, that just the same results are shown in all other cases in which I have been yet able to examine such observations of night temperatures under a clear sky; and the following figures are got from observations made between the 4th and the 25th of March, 1850 (also taken from the Madras records), during which period the sky remained remarkably clear, and great variations of the quantity of vapour took place.

Tension of vapour .....	inch. ·888	·849	·805	·749	·708	·659	·605	·554	·435
Fall of temperature from 6.40 P.M. to 5.40 A.M. ....	Fahr. 6°0	7°1	8°3	8°5	10°3	12°6	12°1	13°1	16°5

The temperature of air at 6<sup>h</sup> 40<sup>m</sup> P.M. varied from 78°·9 to 84°·7 Fahr.

I before observed that the variation of the heating-power of the sun prevented useful comparisons between the increase of heat during the day at different times of the year. But the fact comes out clearly enough that the air, when dry, is more freely traversed by the sun's heat than when damp. The observations of March 1850, arranged so as to bring out this point, give the following results:—

Tension of vapour ....	inch. ·824	·737	·670	·576	·511	·394
Rise of temperature from 5.40 A.M. to to 1.40 P.M. ....	Fahr. 12°4	15°1	19°3	22°2	24°3	27°0

It may be remarked that a possible cause of error in the conclusions drawn from the *nocturnal fall* of temperature, namely the greatly increased depression of temperature of evaporating surfaces in dry air, is clearly shown not to be of weight by the *diurnal rise* of temperature being exaggerated in the dry air



notwithstanding the great depression of evaporating surfaces. During the night hours in March 1850, the mean depression of the temperature of the wet-bulb thermometer varied from  $6^{\circ}\cdot 0$  in the dampest period, to  $9^{\circ}\cdot 9$  in the driest. During the day hours the mean depression varied from  $12^{\circ}\cdot 4$  in the dampest, to  $15^{\circ}\cdot 0$  in the driest. If the cooling of evaporation had any important effect at *night* in *increasing* the *fall* of temperature, it must have acted during the *day* in *diminishing* the *rise* of temperature. But the *rise* was in no sense diminished, but the reverse; therefore it may fairly be inferred that the action of evaporation in causing night cold must be unimportant,—a conclusion which otherwise would seem probable.

I am aware that Dr. Tyndall's researches have indicated that the watery vapour in the air is less effective in impeding the passage of solar heat than that of terrestrial heat. But the facts now noticed seem to show that even on solar heat the effects are important.

It will be understood that these remarks are only intended to indicate conclusions come to on the consideration of a limited field of observations. Should I have an opportunity of finding other facts of a like nature likely to throw further light on this important matter, I shall endeavour to publish them also.

## X. *Proceedings of Learned Societies.*

### ROYAL INSTITUTION OF GREAT BRITAIN.

June 15, “**E**XPERIMENTS on the Vibrations of Strings.” By 1866. John Tyndall, Esq., LL.D., F.R.S., &c.

1. I lay hold of one end of this india-rubber rope, the other end of which is fixed to the ceiling, and by a jerk raise a protuberance upon it. The protuberance runs along the rope to its fixed end, is there reflected, and reversing itself, returns to my hand. In this case, where the points of the rope rise in succession to form the protuberance, we have an example of a *progressive* wave or undulation.

2. After the first wave I now send a second, so that it shall meet the reflected wave on its return. The foremost ends of both waves now meet in the centre of the rope; they there neutralize each other, and the two halves continue to swing with an apparently motionless point called a *node* between them.

3. I now stop the rope, send a wave forward, and then another wave so quickly after it that this second wave shall meet the first at one-third of the length of the rope from its fixed end. At that point a node is produced. But I have already sent a third wave after the second. The second wave being reflected at the node, meets this third one and a second node is formed. The whole rope is now divided into three vibrating parts, separated from each other by two nodes.

4. By properly timing the impulses imparted to the rope I can divide it into four, five, six, ten, and even twenty vibrating parts



separated from each other by the appropriate number of nodes. With a certain rapidity of vibration on the part of my hand I cause the rope to swing to and fro as a whole. Twice that rapidity divides it into two equal vibrating parts; three times that rapidity into three vibrating parts, and so on. The number of vibrating parts, or *ventral segments*, as they are called, is in fact directly proportional to the rapidity of my hand's vibration.

5. In these cases, where every point of every ventral segment moves to and fro at the same time, we have examples of *stationary undulations*.

6. My hand, which produces this vibration, does not move through more than half an inch of space, while the ventral segments oscillate through a space of four-and-twenty. This wide vibration is in fact produced and maintained by the addition together of small impulses properly timed. The nodes, moreover, though apparently motionless, are not strictly so; for if they were, the vibration of the segments would soon come to an end. In fact, it is by the motion transmitted through the nodes that the vibrations of the rope are sustained.

7. I might attach the free end of this rope to any suitable vibrating body instead of taking it in my hand. If the rate of vibration of the body were that of any aliquot part of the rope, it would divide itself accordingly.

8. The effect may also be produced by causing the vibrations of an aliquot part of our rope to excite vibrations in the remaining portion. Stretched vertically from top to bottom of this wooden frame is an india-rubber tube. I encircle the middle of the tube with the finger and thumb of my left hand, and pull the lower half aside with my right. The lower half vibrates, but the upper half vibrates also. In fact the small amount of play permitted by my hand has enabled the pulse to transmit itself, to be reflected, and to accumulate its motion to this extent. I withdraw my left hand: the tube continues to vibrate in two equal parts, divided from each other by a node.

9. I encircle the tube at one-third of its length from the lower end, and pull aside the shorter segment; it vibrates more quickly than the half tube, and the vibration immediately causes the upper and longer portion to divide into two equal parts. I now withdraw my hand, and the tube continues to vibrate in three equal segments, which are separated from each other by two nodes.

10. In like manner I encircle the tube at one quarter of its length from its lower end, and pull the lower and shorter segment aside; it vibrates, and forthwith the longer segment above divides into three vibrating parts. I now withdraw my hand, and the tube continues to oscillate in four equal segments, separated from each other by three nodes.

11. Again, from side to side of the room is stretched this stout iron wire 24 feet long. I seize the wire at the point which divides it into two parts, one three times as long as the other, and pulling the shorter segment aside permit it to vibrate; the remaining portion of the wire divides itself into three ventral segments. I

have placed silvered beads at the nodes and at the centres of the vibrating segments; you see the light shining from those beads, and you notice that while the nodal beads remain stationary, the others describe luminous lines.

12. If I place sheets of paper across the wire at the nodes and at the ventral segments, on causing it to vibrate thus, the sheets placed across the ventral segments are tossed off, while those at the nodes remain undisturbed.

13. From these effects which you can actually see, I might pass on to vibrating strings, and show you that they divide themselves similarly. I might also show you that it is hardly possible for a musical string to vibrate as a whole without having these smaller vibrations riding like parasites upon the large one. The addition of these smaller vibrations gives *quality* or *timbre*, or, as the Germans call it, *Klangfarbe* to the note. They constitute the harmonics of the string.

14. In this vice is fixed upright a rod of iron 4 feet long. I pull it aside and it vibrates as a whole; its vibrations are rendered more distinct by casting its shadow upon a white screen. I now strike the rod sharply at a point about one-third of its length from its fixed end. The pulse runs along the rod, returns from its free end, and is met by the succeeding pulses; and now the rod is divided into two vibrating parts—a whole segment and a half segment, separated from each other by this dark motionless node. By promptly striking the rod lower down, I cause it to divide into two complete vibrating segments, forming those shadowy spindles upon the screen, and half a segment at the top, which spreads out like a fan. The nodes are marked by the two dark points where the shadow is complete.

15. This production of stationary undulations on a large scale through the combination of direct and reflected waves, for the illustration of which we are mainly indebted to the brothers Weber, forms a fit introduction to the experiments of M. Melde of Marburg, who has obtained a series of very beautiful effects by associating with vibrating bodies suitably stretched strings.

16. In M. Melde's first experiment he stretched a string across a bell, or belljar, from edge to edge: when the bell was caused to vibrate, the string vibrated also. By varying the tension of the string it was caused to vibrate as a whole, or to divide itself into two, three, four, five, or more vibrating parts, separated from each other by the appropriate number of nodes.

17. He then attached his strings to tuning-forks, and obtained the same effect in a more marked and beautiful manner. To this tuning-fork I have attached a silk string which passes round a distant peg, by turning which the string is stretched. The length of the string is 8 feet. The tension of the present moment is such that when the fork is caused to vibrate, the string swings as a whole, its periods of vibration being synchronous with the impulses imparted to it by the fork. We have here a beautiful gauzy spindle produced by the silk, fully 6 inches wide at its point of greatest amplitude.

18. The motion of the end of the string in contact with the fork is hardly sensible; and still through this apparently motionless part of the string the whole of its motion is transmitted.

19. I relax the string by turning the peg, and now it suddenly divides itself into two ventral segments, separated from each other by a node. When the synchronism between the fork and string is perfect, the vibrations of the string are steady and long continued; but a slight departure from synchronism introduces unsteadiness, and the vibrations, though they may show themselves for a time, quickly disappear.

20. I relax the string still further; it now divides itself into three vibrating parts; relaxing still further, it divides into four vibrating parts; and thus I might continue to subdivide the string into ten or even twenty equal parts, separated from each other by a number of nodes one less than the number of ventral segments.

21. In the arrangement now before you, the fork vibrates in the direction of the length of the string; its tendency, therefore, is to throw the string into longitudinal vibration. But, in fact, every forward stroke of the fork raises a protuberance upon the string, which runs to its fixed end and is there reflected, so that when the longitudinal impulses are properly timed, they produce a transverse vibration. I take a heavy string in my hand, stretch it, and move my hand to and fro in the direction of the string. It vibrates as a whole, and I notice that it is always when the string is at the two limits of its excursion that my hand moves forward. If the string vibrate in a vertical plane, my hand, in order to time the impulses properly, must move forward at the moment the string reaches the upper and also at the moment it reaches the lower limit of its excursion. A little reflection will make it plain that, in order to accomplish this, my hand must execute a complete vibration while the string executes a semi-vibration\*; in other words, the vibrations of my hand must be exactly twice as rapid as those of the string.

22. Precisely the same must be true of a tuning-fork to which a proper string is attached. When the fork vibrates in the direction of the string, the number of complete vibrations which it executes in a certain time will be twice the number executed by the string.

23. If in this case the fork and string vibrate with sufficient rapidity to produce musical notes, the note of the fork will be an octave above that of the string. That it is so, has been proved by M. Melde's direct observations.

24. Taking hold of the end of this heavy string, I cause my hand to move to and fro, not in the direction of the string, but at right angles to that direction. The string now swings as a whole in a vertical plane. Here every upward movement of my hand coincides with an upward movement of the string, every downward movement of my hand with a downward movement of the string. In fact the vibrations of hand and string in this case synchronize perfectly; and if the hand could emit a musical note, the string would emit a

\* A complete vibration, it will be borne in mind, consists of one complete excursion to *and fro*. A semi-vibration, on the contrary, consists of an excursion from one limit of the vibration to the other.



note of the same pitch. The same holds good when a vibrating fork is substituted for the vibrating hand. While, therefore, when the vibrations are longitudinal a complete vibration of the fork synchronizes with a semi-vibration of the string, when the vibrations are transversal, a complete vibration of the fork corresponds to a complete vibration of the string.

25. Hence, if the string vibrate as a whole when the vibrations are longitudinal, it will divide itself into two ventral segments when the vibrations are transversal; or, more generally expressed, preserving the tension constant, whatever be the number of ventral segments produced by the fork when its vibrations are longitudinal, twice that number are produced when the vibrations are transverse. Here, for example, is a string 8 feet long, vibrating longitudinally; the fork divides the string into four equal vibrating parts. I place the fork so that it shall vibrate at right angles to the string. The number of ventral segments is now eight, or double the former number. This result was amply illustrated by the experiments of M. Melde.

26. Attaching two strings of the same length to the two prongs of the same fork, stretching one string in the direction of the prongs, and the other at right angles to that direction, and subjecting the strings to the same tension, when the fork is caused to vibrate, the one string divides itself into double the number of vibrating segments exhibited by the other.

27. When white silk strings vibrate thus, the beauty of the ventral segments is extreme. The nodes appear white and fixed, while the vibrating parts form delicate gauzy spindles in the air; every protuberance of the twisted string writes its motion in a more or less luminous line on the surface of the aerial gauze.

28. Certain twisted strings do not adhere to the same plane. They vibrate simultaneously in two rectangular directions, and every one of their points describes a closed curve. When the two vibrations are of the same amplitude, and have the proper difference of phase, the ventral segments describe surfaces of revolution.

29. The path described by the various points of the string may be studied, after the manner of Dr. Young, by throwing light upon them and watching the lines described by the illuminated points. By twisting a flat and burnished silver wire we form a spiral surface, from which at regular intervals the light flashes when the whole wire is illuminated. Attaching the wire to a tuning-fork and causing it to vibrate, its luminous spots describe luminous lines. If the wire vibrate as a whole without any sensible admixture of its harmonic divisions, these spots describe straight lines, which are drawn brilliantly across the ventral gauze; but when, by slackening or tightening the wire, other vibrations are caused to mingle with the fundamental one, the combination of vibrations expresses itself in luminous scrolls of extraordinary beauty.

30. But to see this beauty you must be close to it. The vibrating segments of our silk strings were, I fear, also too faint to be seen at a distance. For the silk string I substitute a fine platinum wire, which now stretches from this tuning-fork over a bridge of copper, and then round a peg. I send an electric current through



the wire, which now glows brightly. I sound the fork: the wire vibrates as a whole; its two ends are brilliant, but its middle is chilled by its rapid passage through the air. Thus you have a shading off of incandescence from the ends to the centre of the wire. I relax the tension: the wire now divides itself into two vibrating parts; I relax still further and obtain three; still further, and now you have the wire divided into four ventral segments separated from each other by these three brilliant nodes. Right and left from every node the incandescence shades away until it disappears. You notice also that when the wire settles into steady vibration the nodes shine out more brilliantly than the wire shone before the vibration commenced. This is due to the cooling of the vibrating segments. When they are chilled by their swift passage through the air, their conductivity is improved. More electricity passes through the vibrating than through the non-vibrating wire, and hence the augmented glow of the nodes.

31. Certain twisted cords, as I have said, when attached to tuning-forks execute circular instead of plane vibrations. Circular vibrations may always be obtained by attaching one end of a string to a rotating point, and timing the velocity of rotation to suit the periods of vibration possible to the string.

32. Thus, suspended from the ceiling is this white cotton rope, the lower end of which is attached to a hook belonging to this whirling table. When this handle is turned the hook rotates, describing a circle less than an inch in diameter. By properly regulating the velocity of rotation I cause the rope to divide into a series of spindles, which appear like grey gauze when projected against a dark background. I can cause the number of these spindles to vary from one to twenty, by varying the velocity of rotation.

33. In this experiment the rope is vertical and the rotating wheel horizontal; but I have here an arrangement in which the wheel is vertical and the vibrating chord horizontal. Instead of a rope I now employ a burnished silver chain. Turning this wheel slowly, I cause the chain to swing as a whole, and describe a spindle 12 feet long and nearly 2 feet in diameter at its widest part. Augmenting the speed of rotation I divide the chain into two spindles, each 6 feet long and more than a foot in diameter; a still higher velocity gives us three spindles, a still higher four, and so on. The gas-light here flashes at intervals from the burnished links of the chain, and each of those brilliant points describes a curve of light.

34. As soon as synchronism is established between the wheel and the chain, the amount of work performed by the arm which turns the wheel is very sensibly augmented. Indeed it may be augmented until the strain thrown upon the chain by the accumulation of small impulses is sufficient to break it.

35. I substitute for the chain this lighter cotton rope, round which a silver band has been coiled as a spiral; and from an electric lamp placed at the end of the rope I send a beam of light along its entire length. I now turn the wheel and divide the rope successively into two, three, four, or five ventral segments. The spindles show a graduated brilliancy, which is intensified until it becomes almost daz-

zling at the nodes. The vibrating chord is indeed better seen when the light that falls upon it has been caused to pass through coloured glass. We thus obtain at pleasure green, blue, and red spindles, with nodes like fire shading off into the more subdued light of the ventral segments.

36. Substituting for the cotton rope a string of silvered beads 12 feet long, I send the beam from the electric lamp along the string. On every bead rests a spot of light of sunlike brilliancy. When the wheel is turned, each spot describes a circle, and every ventral segment, of which we have now four, seems formed of a series of such dazzling parallel rings, which diminish in size right and left from the points of maximum amplitude till the diameters vanish at the nodes.

37. So much for physical beauty; we have now to revert to beauty of another kind. The experiments with tuning-forks above described may be extended to the establishment of all the laws of vibrating strings. I have here four forks, *a*, *b*, *c*, *d*, whose vibrations are in the proportion of the numbers 1, 2, 4, 8. Attaching a string 8 feet long to the largest fork, I stretch it by a weight which causes it to vibrate as a whole. Keeping the stretching weight or tension the same, I attach pieces of the string to the other forks, and determine in each case the length which swings as a whole. These lengths are in the ratio of 8, 4, 2, 1.

38. *Hence the rapidity of vibration is inversely proportional to the length of the string.*

39. Here the string 8 feet long vibrates as a whole when attached to the fork *a*. I now transfer it to *b*, still keeping it stretched by the same weight. It vibrates when *b* vibrates; but how? By dividing into two equal ventral segments. In this way alone can it accommodate itself to the vibrating period of *b*. Attached to *c*, the same string separates into four, while when attached to *d* it divides into eight ventral segments. This may be deduced immediately from the law enunciated in 38, and its experimental realization reacts as a proof of that law.

40. This result admits of extension. I have here two tuning-forks separated from each other by the musical interval called a fifth. Attaching a string to one of the forks I stretch until it divides into two ventral segments; attached to the other fork and stretched with the same weight, the string divides instantly into three segments when the fork is set in vibration. Now to form the interval of a fifth the vibrations of the one fork must be to those of the other in the ratio of 2 : 3. The division of the string therefore declares the interval. Here also are two forks separated by an interval of a fourth. With a certain tension one of the forks divides our string into three ventral segments; with the same tension the other fork divides it into four, which two numbers express the ratio of the vibrations. In the same way the division of the string in relation to all other musical intervals may be illustrated.

41. Again. Here are two tuning-forks, *a* and *b*, one of which (*a*) vibrates twice as rapidly as the other. I attach this string of silk to *a*, and stretch the string until it synchronizes with the fork and vibrates as a whole. I now form a second string of silk of the same

length by laying four strands of the first side by side. I attach this compound thread to *b*, and, keeping the tension the same as in the last experiment, set *b* in vibration. The compound thread synchronizes with *b*, and swings as a whole. Now by quadrupling the original thread, I obtained a string of twice the diameter of the original one; for the transverse section of any string is as the square of its diameter. Hence, as the fork *b* vibrates with half the rapidity of *a*, by doubling the diameter of the string, I halved its rapidity of vibration. In the same simple way it might be proved that by trebling the diameter of the string we reduce the number of its vibrations to one third. In general terms:—

42. *The rapidity of vibration is inversely proportional to the diameter of the string.*

43. A beautiful confirmation of this result is thus obtained:—Attached to this tuning-fork is a silk string 6 feet long. Two feet of this string are composed of four strands of the single thread placed side by side, the remaining 4 feet are a single thread. I apply a tension which causes the string to divide into two ventral segments. But how does it divide? Not at its centre, as is the case when the string is of uniform thickness throughout, but at the point where the thick string terminates. This thick segment 2 feet long is now vibrating at the same rate as the thin segment 4 feet long, a result which must manifestly follow from the combination of the two laws which we have already established. I need hardly say that if the lengths were in any other ratio than 1 : 2, the node would not be formed at the point of union of the two strings.

44. We have now to establish the third law of vibrating chords. Here are two strings of the same length and thickness. One of them is attached to the fork *b*, the other to the fork *a*, which vibrates with twice the rapidity of *b*. Stretched by a weight of 20 grains placed on this balanced scale-pan, the string attached to *b* vibrates as a whole. Substituting the fork *a* for *b*, I find that a weight of 80 grains causes the string to vibrate as a whole. Hence to double the rapidity of vibration we must quadruple the stretching weight. In the same way it might be proved that to treble the rapidity of vibration we should have to make the stretching weight nine-fold. In general terms:—

45. *The rapidity of vibration is proportional to the square root of the tension.*

46. In the foregoing experiment both the tension and the rate of vibration were caused to vary. We will now cause the tension alone to vary, and observe the effect upon the entire string. I carry this silk chord from this tuning-fork to the scale-pan, and stretch it by a weight of 80 grains. The string vibrates as a whole. By diminishing the weight I relax the string, which finally divides sharply into two ventral segments. What is now the stretching weight? 20 grains. With a stretching weight of almost exactly 9 grains it divides into three segments, while with a stretching weight of 5 grains it divides into four segments. Thus then a tension of one-fourth doubles, a tension of one-ninth trebles, a tension of one-sixteenth quadruples the number of ventral segments. In general terms, the



number of segments is inversely proportional to the square root of the tension. This result may be deduced by reasoning from the laws enunciated in 38 and 45, and its realization in fact confirms their correctness\*.

47. Finally, I have here three wires of the same length and thickness, but of very different densities; one of them is of the light metal aluminium, another of silver, and another of the heavy metal platinum. I attach the wires in succession to this tuning-fork, and determine the weights necessary to cause them to vibrate as a whole, or to form the same number of ventral segments. The stretching weights here necessary I find [to be directly proportional to the specific gravities of the wires. From this result, combined with that enunciated in 45, it follows that—

48. *The rapidity of vibration of different chords of the same length and thickness is inversely proportional to the square root of their densities.*

49. It is perhaps worth remarking, that, by means of a tuning-fork, the specific gravities of all metals capable of being drawn into wires of sufficient fineness and tenacity may be determined.

The foregoing laws have been combined in various ways; and the deductions drawn from them, when subjected to the test of direct experiment, have in every instance been verified.

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#### ROYAL SOCIETY.

[Continued from vol. xxxi. p. 545.]

April 12, 1866.—Lieut.-General Sabine, President, in the Chair.

The following communication was read:—

“On Uniform Rotation.” By C. W. Siemens, F.R.S.

The paper sets out with an inquiry into the conditions of the conical pendulum as a means of obtaining uniform rotation. This instrument, as applied by Watt to regulate the velocity of his steam-engines, is shown to be defective,—first, because the regulated position of the valve depends upon the angular position of the pendulums, and therefore upon the velocity of rotation, which must be permanently changed in order to effect an adjustment of the valve; and secondly, because when the balance between force and resistance of the engine at a given velocity is disturbed, the angular position of the pendulums will not change until a power has been created in them, through acceleration of the engine, sufficient to overcome the mechanical resistance of the valve—giving rise to a series of fluctuations before a balance between the power and resistance of the engine is reestablished.

These defects in Watt’s centrifugal governor are shown to be obviated in the chronometric governor, an instrument which was proposed by the author of the paper twenty-three years ago, and which consists of a conical pendulum proceeding at a uniform angle of rotation, and therefore at uniform speed, which is made to act upon the regulating-valve by means of a differential motion between itself and the engine to be regulated, which latter has to accommo-

\* This experiment, in whole or in part, has been already performed by Professor Foster, of University College.



date itself to the rotations imposed by the independent pendulum. The differential-motion wheels are taken advantage of for imparting independent driving- or sustaining-power to the pendulum; and a constancy of the angle of rotation, notwithstanding unavoidable fluctuations in the sustaining-power, is secured (within certain limits) by calling into play a break, or fluid resistance, at the moment when the angle of rotation reaches a maximum, which maximum position is perpetuated by increasing the sustaining-power beyond what is strictly necessary to overcome the ordinary resistance of the pendulum.

The chronometric governor is used by the Astronomer Royal to regulate the motion of the large equatorial telescope and recording apparatus at Greenwich, in which application a very high degree of regularity is attained; but the instrument proved to be too delicate in its adjustments for ordinary steam-engine use.

After a short allusion to M. Foucault's governor, the paper enters upon the description of a new apparatus which the writer has imagined for obtaining uniform rotation, notwithstanding great variations in the driving-power, and which consists, in the main, of a parabolic cup, open at top and bottom and mounted upon a vertical axis, which cup dips with its smaller opening into a liquid contained within a casing completely enclosing the cup. It is shown that a certain angular velocity of the cup will raise the liquid (entering from below) in a parabolic curve to its upper edge or brim, and that a very slight increase of the velocity will cause actual overflow, in the form of a sheet of liquid, which, being raised and projected against the sides of the outer chamber, descends to the bath below, whence fresh liquid continually enters the cup. Without the overflow scarcely any power is required to maintain the cup, with the liquid it contains, in motion; but the moment an overflow ensues, a considerable amount of power is absorbed in raising and projecting a continuous stream of the liquid, whereby further acceleration is prevented, and nearly uniform velocity is the result. When absolute uniformity is required, the cup is not fixed upon the rotating axis, but is suspended from it by a spiral spring, which not only supports its weight, but also transmits the driving-power by its torsional moment. The cup is guided in the centre upon a helical surface, which arrangement has for its result that an increase of resistance or of driving-power produces an increased torsional action of the spring, and with it an automatic descent of the cup, sufficient to make up for the thickness of overflow required to effect the readjustment between power and resistance, without permanent increase of angular velocity.

It is shown that the density of the liquid exercises no influence upon the velocity of the cup, which velocity is expressed by the following formula,

$$n = \frac{\sqrt{2gh\left(1 + \frac{\rho^2}{r^2 - .293\rho^2}\right)}}{2r\pi}$$

in which  $n$  signifies the number of revolutions per second,  
 $h$  the height of liquid from the surface to the brim of cup,  
 $r$  the radius of the brim, and  
 $\rho$  the radius of lower orifice of cup;

only the rigidity of the spring must be greater when a comparatively dense liquid is employed.

In order to test the principle of action here involved, Mr. Siemens has constructed a clock consisting of a galvanic battery, an electro-magnet, and his gyrometric cup, besides the necessary reducing-wheels and hands upon a dial face, which proceeds at a uniform rate, although the driving-power may be varied between wide limits, by the introduction of artificial resistances into the electrical circuit. The instrument appears, therefore, well calculated for regulating the speed of all kinds of philosophical apparatus, and also for obtaining synchronous rotations at different places for telegraphic purposes. One of its most interesting applications is embodied in the "Gyrometric Governor" for steam-engines, of which an illustration is given. This consists of a cup of 200 millimetres diameter and the same height, which is fixed upon its vertical axis of rotation, and is enclosed in an outer chamber, containing water in such quantity that the lower extremity of the cup dips below its surface. The upper edge of the rotating cup is, in this application, surrounded by a stationary ring armed with vertical vanes, by which the overflowing liquid is arrested and directed downward, causing it to fall through a space or zone which is traversed by a number of radial and vertical blades projecting from the external surface of the rotating cup, which, in striking the falling liquid, project it with considerable force against the sides of the outer vessel, at the expense of a corresponding retarding effect on the cup, increasing its regulating-power.

The cup-spindle carries at its lower extremity a pinion, which gears into two planet-wheels at opposite points, which on their part gear into an inverted wheel surrounding the whole, which latter is fastened upon a vertical shaft in continuation of the cup-spindle, and is driven round by the engine in the opposite direction to the motion of the cup. The two intermediate or planet-wheels are attached to a rocking frame supported, but not fixed, upon the central axis, which wheels, in rotating upon their studs, are also free to follow the impulse of either the pinion or the inverted wheel to the extent of the differential motion arising between them. The rocking frame is connected to the regulating valve of the engine, and also to a weight suspended from a horizontal arm upon the valve-spindle, tending to open the valve and at the same time to accelerate the cup to the extent of the pressure produced between the teeth of the planet-wheels and the pinion, while the engine is constantly employed to raise the weight and to cut off the supply of steam. The result is that the engine has to conform absolutely to the regular motion imposed by the cup, which will be precisely the same when the engine is charged with its maximum or its minimum of resisting load.

The paper shows that the action upon the valve must take place at the moment when the balance between the power and load of the engine is disturbed, and that the readjustment will be effected notwithstanding a resistance of the valve exceeding 100 kilogrammes—a result tending towards the attainment of several important objects.

XI. *Intelligence and Miscellaneous Articles.*

## OBSERVATIONS ON SKYLIGHT POLARIZATION AT PHILADELPHIA.

BY MR. CHASE.

RECENT observations with a Savart polariscope having led me to results which, while generally confirmatory, differ in a few particulars from those published by Sir David Brewster (*Philosophical Magazine*, S. 4. vol. xxx. pp. 118 and 166 *et seq.*), I place some of them on record to facilitate a comparison with similar observations at other places.

1. In all the great circles which pass through the sun the polarization of a clear sky is positive, except in the neighbourhood of the solar and antisolar points. If the polariscope is rotated from the positive maximum, the bands gradually diminish in brilliancy, vanishing at about  $45^\circ$ , and attaining a negative maximum at about  $90^\circ$ .

2. Within the primary lemniscates, of which the solar and antisolar points are the respective centres, and the neutral points (actual or theoretical\*) are the limits, the polarization of a clear sky is negative when the bands pass towards the sun's centre, vanishing when the bands are inclined  $45^\circ$  to the solar radii, and attaining a positive maximum when the inclination reaches  $90^\circ$ .

3. Arago's and Babinet's neutral points can be seen as well before sunrise as after sunset, provided the atmospheric conditions are the same. Brewster gives the preference to the evening observation, but apparently for no other reason than that the sky is then generally clearer than in the morning. (Vol. cit. p. 118.)

4. I have repeatedly, and with little comparative difficulty, observed Brewster's neutral point. In the majority of cases, when the sun's altitude has been sufficient, I have been able to fix its position with nearly as much facility as that of Babinet's. (For the difficulties of Brewster and Babinet, see *loc. cit.* pp. 119, 166, 181.)

5. Within the solar primary lemniscate it is frequently difficult to make any ordinary observation of the polarized bands, on account of the dazzling intensity of the light. But when the direct rays of the sun have been shut off by a thin disk (placed with its edge towards the eye, so that the polarization will not be affected by reflexion from the surface of the disk), I have often been able to mark the opposite polarizations and the position of the neutral points with perfect ease, even at midday.

6. In our climate it is by no means unusual to have days on which all the three neutral points can be observed, and their places determined. During the whole period of Brewster's observations at St. Andrews he found but two such days, April 5 and 8, 1842 (*loc. cit.* pp. 124, 163).

7. Quasi neutral lines, dividing bands of opposite polarization, can be found in nearly all parts of the sky by rotating the polariscope  $45^\circ$  from the line of maximum positive or negative polarization.

\* There is one *theoretical* neutral point below the antisolar point. It is probably never above the horizon when there is light enough to determine its position.



But a slight additional rotation will show that the neutralization is only apparent.

8. The position of a true neutral point can be determined by sweeping its neighbourhood alternately with the vertical and with the horizontal bands, and marking the intersection of the lines of vanishing polarization.

9. In consequence of the arrangement of the lines of equal polarization, when the sky is swept with a polariscope for a few degrees on each side of a neutral point, the line which separates the oppositely polarized bands forms curves with a convexity determined by the position of the sun or the antisolar point\*.

10. Some of my observations have indicated an apparent correlation between these curves and the magnetic dip and terrestrial latitude. I have not been able to satisfy myself whether this correspondence was merely accidental, or whether it indicated another point of analogy between the laws of light and magnetism.

11. The varying effects of haze or cloud appear, on the whole, to confirm Brewster's theory that the neutral point is produced "by the opposite action of light polarized by reflexion and refraction." (See pp. 123, 169, 176, 178, 180.)

12. In one instance, soon after sunset, the reflexion from scattered clouds in the neighbourhood of the antisolar point was such as to totally eclipse Arago's neutral point, the polarization being positive over the entire arch, from Babinet's neutral point to the eastern horizon.—*Proceedings of the American Philosophical Society*, vol. x. January 5, 1866.

#### ON MOTION IN A RESISTING MEDIUM.

BY DR. O. SCHRECK OF BREMEN.

A series of experiments were made by filling a tall vessel with water, and allowing bodies to fall in it. From the space fallen through and the time occupied, an approximate conclusion could be drawn as to the resistance of the liquid. The results are as follows:—

(1) With velocities up to 20 centimetres the resistance is proportional to the square of the velocity.

(2) With greater velocities it is proportional to a higher power of the velocity, which increases with the increase of the resisting surface.

(3) The resistance to spheres is approximately proportional to the square of the diameter of the sphere, but, with larger spheres, increases with the diameter in a continually increasing ratio.

(4) The resistances to spheres and cylinders of the same diameter are as 2 : 3.

(5) A cone experiences greater resistance than a sphere of the same diameter.—*Poggendorff's Annalen*, April 1866.

\* I am not aware whether this is the "singular effect" thus described by Brewster (*loc. cit.* p. 124):—"In carrying the bands vertically round, the neutral line, in place of crossing them at a right angle, was the arc of a circle, to which one of the bands was a tangent." (See also pp. 121, 167.)





Fig. 2



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XII. *Flame Reactions.* By R. BUNSEN\*.

[With a Plate.]

ALMOST all the reactions which can be performed by means of the blowpipe may be accomplished with far greater ease and precision in the flame of the non-luminous gas-lamp. This flame, moreover, possesses several peculiarities which render it available for reactions by which the smallest traces of many substances occurring mixed together can be detected with certainty when the blowpipe and even still more delicate methods fail.

The number of new reactions which can in this way be performed is so large that I am only able here to mention the most important, leaving it to those who wish to make themselves acquainted with this subject to apply the same principles to other cases, and to follow out this method in other directions.

I. THE STRUCTURE OF THE NON-LUMINOUS GAS-FLAME.

The gas-lamp with non-luminous flame used for these reactions is represented in fig. 1, Plate I., and must be made, exactly to scale,  $3\frac{1}{2}$  times as large as the drawing. It must be furnished with a cap at *a* for closing and opening the draught-holes, so as to be able to regulate the supply of air for every dimension of the flame. The conical chimney *dddd*, fig. 2, must also be made of such a size that the flame burns perfectly steady.

Fig. 2 represents this flame of its natural size. It is composed of the following three chief divisions:—

A. *The dark cone, a a a*, containing the cold unburnt gas mixed with about 62 per cent. of atmospheric air.

B. *The flame-mantle, a c a b*, formed of the burning coal-gas mixed with air.

\* Translated by Professor Roscoe, F.R.S., from the *Annalen der Chemie und Pharmacie*, vol. cxxxviii. p. 257.

C. *The luminous point, a b a*, not seen when the lamp is burning with the draught-holes open, but obtained of the size required for the reactions by closing these holes up to a certain point.

The following six points in the flame are used in the reactions :—

(1) *The base of the flame* lies at  $\alpha$ ; its temperature is comparatively very low, as here the burning gas is cooled by the upward current of cold air, and much heat is absorbed by the cold end of the metal tube. If mixtures of flame-colouring substances are held in this part of the flame, it is often possible to vaporize the most volatile constituent, and thus in the first few moments to obtain tints which cannot be observed at higher temperatures, because they then become masked by colours produced by the volatilization of the remaining substances.

(2) *The zone of fusion* lies at  $\beta$ , somewhat above the first third of the flame in height, and midway between the inner and outer limits of the mantle at the point where the flame is thickest. This is the point in the flame which possesses the highest temperature, and it is therefore used in testing substances as regards their melting-point, their volatility, emissive power, as well as for all processes of fusion at high temperatures.

(3) *The lower oxidizing flame* lies at  $\gamma$ , in the outer margin of the zone of fusion, and is especially suitable for the oxidation of substances dissolved in beads of fused salts.

(4) *The upper oxidizing flame* at  $\epsilon$  is formed by the highest point of the non-luminous flame, and acts most powerfully when the draught-holes of the lamp are wide open. This flame is suited for the oxidation of larger portions of substance, for roasting off volatile oxidation-products, and generally for all those cases of oxidation in which an excessively high temperature is not needed.

(5) *The lower reducing flame* lies at  $\delta$ , on the interior edge of the mantle next to the dark central zone. As the reducing gases at this point are mixed with unburnt atmospheric oxygen, many substances remain here unaltered which become deoxidized on exposure to the upper reducing flame. This point of the flame gives, therefore, very valuable reactions which cannot be obtained with the blowpipe. It is especially available for reductions on charcoal, and in beads of fused salts.

(6) *The upper reducing flame* is formed by the luminous point  $\eta$ , produced over the dark zone when the admission of air is lessened by the gradual closing of the draught-holes (fig. 1, *a*). If this luminous point is made too large, it will be found that a test-tube filled with cold water becomes covered with a film of lamp-black: this never ought to occur. This flame contains no free oxygen, is rich in finely divided incandescient carbon, and hence it possesses far more powerful reducing-powers than the lower



reducing flame. It is especially available for reducing metals when it is desired to collect them in the form of films.

## II. METHOD OF EXAMINATION IN THE VARIOUS PARTS OF THE FLAME.

### *A. Behaviour of the Elements at High Temperatures.*

This is one of the most important reactions which can be employed for the detection and separation of substances. The possibility of producing, with the flame of the lamp alone, a temperature as high as or higher than that of the blowpipe, depends upon the fact that the radiating surface of the heated body be made as small as possible. The arrangement for bringing the substances into the flame must therefore be on a very small scale. The platinum wire upon which the substance is heated must scarcely exceed the thickness of a horsehair, and one decimetre in length of the wire must not weigh more than 0.034 grm. It is impossible to obtain the results hereafter detailed if a thicker wire than this is employed. Substances which act upon platinum, or which will not adhere to the moistened surface of the metal, are held in the flame upon a thin thread of asbestos, of which a hundred may be obtained from one splinter of the mineral. These threads must not exceed in thickness one-fourth of that of an ordinary lucifer-match. Decrepitating substances are ground to the finest powder on the porcelain lamp-plate with the elastic blade (*a*) of the knife (fig. 4), and drawn up on to a moistened strip of one square centimetre of filter-paper. If the paper is then burnt, being held with the platinum forceps, or, better, between two rings of fine platinum wire, the sample remains as a coherent crust, which now may without difficulty be heated in the flame.

If the substance requires to be heated in the flame for a long period, the holder (fig. 5) is used. The arm (*a*) is fastened to the carrier (*A*), so fixed on the stand by a spring (as seen at *B*) that it can be moved both horizontally and vertically. The glass tube (fig. 6) is held on this arm (*a*), and the fine platinum wire fused on to the tube thus held in the flame. The splinters of asbestos are stuck into the glass tube (*b*), which slips into the holder, and may then be moved with the carrier (*A*). The carrier (*B*) carries a spring-clamp for holding test-tubes which have to be heated for a considerable time in a particular part of the flame. The little turntable (*C*) contains nine upright supports to hold the wire tubes (fig. 6) employed in the experiments. By means of these arrangements a particle of the substance under examination is brought into the flame, and its behaviour in the coldest and hottest parts of the flame is ascertained, the substance being examined with a lens after each change of tem-

perature. The following six different temperatures can be obtained in the flame, and these points may be judged of by observing the tints attained by the thin platinum wire :—

1. Below a red heat.
2. Commencing red heat.
3. Red heat.
4. Commencing white heat.
5. White heat.
6. Strong white heat.

It is scarcely necessary to remark that these different temperatures must not be ascertained by the glow of the substances themselves, as the luminosity of different bodies depends not only upon the temperature, but also mainly upon their specific power of emission.

The following phenomena are observed when a sample of a substance is heated :—

1. *Emission of Light.*—The emissive power of substances is ascertained by placing them on the platinum wire in the hottest part of the flame. The sample is of weak emissive power when it is less luminous than the platinum wire, of a mean emissive power when both appear about equally luminous, and of strong emissive power when the intensity of the light which it emits is greater than that from the platinum. Most solid bodies emit a white light, others (as, for instance, erbia) coloured light.

Some bodies, such as many osmium, carbon, and molybdenum compounds, volatilize and separate out finely divided solid matter, which renders the flame luminous. Gases and vapours always exhibit a smaller power of emission than fused substances, and these generally less than solid bodies. The form of the substance under examination must always be noted, as the emissive power depends upon the nature of the surface: thus compact alumina, obtained by slowly heating the hydrate, possesses only a moderate emissive power, whereas the porous oxide prepared by quick ignition of the sulphate possesses a high power of emission.

2. *The melting-point* is determined by using the six different temperatures already mentioned. At every increase of temperature the bead is examined with the lens to see whether the volume is decreased or increased, whether bubbles are given off on melting, whether, on cooling, the bead is transparent, and what changes of colour it undergoes during the action of the heat or on afterwards cooling.

3. *The volatility* is ascertained by allowing equally heavy beads of the substance, placed on a platinum wire, to evaporate in the zone of fusion, and observing the time, by means of a me-

tronome, which the bead takes to volatilize. The point at which the whole of the substance is converted into vapour can be ascertained with great accuracy, often to a fraction of a second, by the sudden disappearance of the coloration of the flame. The platinum wire upon which the substance is weighed is protected from the moisture of the air by insertion in a tube (fig. 7). If we know the weight of the tube and wire, the right weight of substance can easily be attached, either by volatilizing a portion or by fusing some more substance on to the bead, and thus making it lighter or heavier. The experiments are best made with one centigramme of substance. The position in the flame where the highest constant temperature exists can be found by moving a fine platinum wire, fixed on a stand and bent at its point at a right angle, slowly about the zone of fusion, and noting the point where it glows most intensely. The beads to be volatilized are then most carefully brought into the flame at the same distance from the point of this wire. Care must also be taken that the dimensions of the flame do not undergo change from alterations in the pressure of the gas whilst the experiments are going on. As a measure of volatility, it is convenient to take the time needed to evaporate one centigramme of the sodium-chloride. If we call this time  $t_0$ , and the time of volatilization of the same weight of another substance  $t_1$ , the volatility of this substance, compared with that of common salt, is

$$f = \frac{t_0}{t_1}.$$

The following examples are taken from experiments of Dr. Hurtzig, to which I have added the chlorides of cæsium and rubidium :—

	Time of evaporation.	Volatility.
Sodium-chloride . . .	84.25	1.000
Sodium-sulphate . . .	1267.0	0.066
Lithium-carbonate . . .	736.5	0.124
Potassium-sulphate . . .	665.2	0.127
Sodium-carbonate . . .	632.0	0.133
Potassium-carbonate . . .	272.0	0.310
Lithium-chloride . . .	114.0	0.739
Potassium-chloride . . .	65.4	1.288
Sodium-chloride . . .	48.8	1.727
Potassium-bromide . . .	41.0	2.055
Rubidium-chloride . . .	38.6	2.183
Sodium-iodide . . . .	35.7	2.360
Cæsium-chloride . . . .	31.3	2.717
Potassium-iodide . . . .	29.8	2.828

It must not be forgotten that the relations of these numbers

are altered if the temperature of evaporation and the weight of the substance are changed. It is, however, remarkable that an approximate relation appears to hold good, probably a mere accident, between the atomic weights and the volatility of those analogous bodies which are easily evaporated. The following numbers show that the volatility of those haloid compounds which evaporate without residue is directly proportional to their atomic weights: thus if A signify the atomic weight, and F the volatility, we find that the equation  $\frac{F}{A} = \text{const.}$  is nearly true.

	A.	F.	$\frac{F}{A}$ .
Lithium-chloride . .	42.49	0.739	0.0174
Sodium-chloride . .	58.43	1.000	0.0171
Potassium-chloride. .	74.57	1.288	0.0173
Sodium-bromide . .	102.97	1.727	0.0168
Potassium-bromide .	119.11	2.055	0.0173
Rubidium-chloride .	120.82	2.183	0.0181
Sodium-iodide . . .	150.07	2.360	0.0157
Cæsium-chloride . .	168.46	2.717	0.0161
Potassium-iodide . .	166.21	2.828	0.0170

Drops of water, alcohol, ether, and other volatile liquids brought into the flame on the platinum wire do not boil even in the hottest part of the flame, and hence they exhibit under these circumstances the phenomenon of the spheroidal state.

4. *Flame-coloration*.—Many substances which volatilize in the flame may be detected by the peculiar kinds of light which their glowing gases emit. These colorations appear in the upper oxidizing flame when the substance causing them is placed in the upper reducing flame. Mixtures of various flame-colouring substances are tested in the lowest and coldest part of the flame; and here it is often possible to obtain for a few moments the peculiar luminosity of the most volatile of the substances unaccompanied by that of the less volatile constituents.

#### B. *Oxidation and Reduction of Substances.*

In order to recognize substances by the phenomena exhibited in their oxidation and reduction, and to obtain them in a fit state for further examination, the following methods are employed:—

1. *Reduction in glass tubes* is especially employed for the detection of mercury, or for the separation of sulphur, selenium, phosphorus, &c. when in combination with sodium or magnesium. A stock of very thin glass tubes is prepared, each 2 to 4 millims. in width and 3 centims. in length: forty of these are



easily made out of one ordinary-sized test-tube, by softening the glass before the blowpipe, and then drawing it out until the requisite size of tube is obtained. This long tube is then cut up with a diamond into pieces 6 to 8 centims. long, and each of these again divided into two over the lamp, and the closed ends neatly rounded. The sample having been finely powdered with the knife-blade (fig. 4, *a*) on the porcelain plate (fig. 3), is treated in a tube either by itself, or with a mixture of carbon and soda, or with sodium or magnesium. A piece of magnesium wire a few millims. in length is for this purpose pushed down into the powdered sample contained in the glass tube; the sodium is carefully freed from rock-oil and rolled out between the fingers to a small cylinder, which is then surrounded by the powdered substance. The best form of carbon is the soot from turpentine, which has been deposited upon the outside of a basin filled with cold water. As soon as the small tube containing the perfectly dry sample has been heated to the point of fusion of the glass, when generally an ignition inside the tube is noticed, it is allowed to cool and then placed upon the porcelain plate, covered by a piece of paper and crushed to powder with the knife, for the purpose of further examining the products of reduction.

2. *Reduction on splinters of Charcoal*.—In this way the metal can be obtained in small globules, or as a porous mass, from quantities often less than a milligramme of the sample.

A transparent crystal of sodium-carbonate is brought near to the outside of the flame, and a common wooden lucifer-match then rubbed over two-thirds of its length with the drops of fused salt. If the match is then turned upon its axis through the flame, the carbonized wood becomes surrounded with a crust of solid sodium-carbonate, which, on heating in the zone of fusion, melts and is absorbed by the carbon. A splinter of charcoal is thus obtained, which is prevented from burning by its glaze of soda. A mixture of the substance is then made with the knife upon the hand with one drop of the melted soda-crystal, and a portion of this, of the size of a mustard-seed, placed upon the point of the splinter. As soon as this has been melted in the lower oxidizing flame, it is passed through a part of the dark interior zone to the hotter portion of the lower reducing flame. The point at which the reduction occurs is easily seen by the violent effervescence of the soda; and this is after a time stopped by bringing the splinter into the dark zone. In order to isolate the reduced metal, the end of the splinter is broken off and rubbed up with a few drops of water in a small agate mortar, when the metallic particles are generally visible without removal of the carbon. For further examination, the carbon and soda can be easily removed by several careful washings, and the particles transferred

to a small piece of curved glass cut out from an old flask\*, in which they are again washed by decantation, the last drops of water removed by suction with a piece of filter-paper, and the metallic particles dried at a moderate heat. A few tenths of a milligramme of the metal is generally sufficient to yield a solution with which all the characteristic precipitations can be accomplished, the reagents being contained in capillary glass threads, dropped into the solution by the milligramme, and the effect thus produced ascertained by examination with a lens. Iron, cobalt, and nickel, which do not fuse to globules on the splinter, are withdrawn from the agate mortar by means of the point of the magnetized blade (fig. 4, *b*), washed with water, and dried high above the flame on the point of the knife. If the blade be then tightly drawn between the upper part of the thumb and the lower part of the first finger, and if the point of the blade be then approached to the metallic particles on the finger, they jump from the hand to the blade, forming a brush-like bundle which can be conveniently examined by the lens, and by touching with a melted borax-bead can be transferred in suitable quantities. The portion of metal remaining on the knife is rubbed on to a small piece of filter-paper, a drop of acid added, and the paper warmed over the flame so as to allow the metal to dissolve; this solution can then be further examined with various reagents.

3. *Films upon Porcelain*.—Those volatile elements which are reduced by carbon and hydrogen can be deposited from their compounds as films on porcelain either in the elementary state or as oxides. Such films can be extremely easily converted into iodides, sulphides, and other compounds, and thus may be made to serve as most valuable and characteristic tests. The films are composed in the centre of a thicker layer, which on all sides gradually becomes thinner until the merest tinge is reached; it is therefore necessary to distinguish between “thick” and “thin” parts of the films. Both exhibit in their variation of thickness all the tints of colour characteristic of the substance under different circumstances of division. One-tenth up to one milligramme is in many cases sufficient for these reactions. Many surpass Marsh’s arsenic test in delicacy and certainty, and approach in this respect the spectrum-analytical methods.

The following films can be obtained:—

(a) *Metallic films* are prepared by holding in one hand a particle of the substance on an asbestos-thread in the upper reducing flame, which must not be too large, whilst with the other hand a glazed porcelain basin, 1 to 2 decimetres in diameter, filled with cold water, is held close above the asbestos-thread in the upper reducing flame. The metals separate out as dead-black

\* Watch-glasses crack much too readily to be used for such experiments.

or brilliantly-black films of varying thickness. Even lead, tin, cadmium, and zinc yield in this way films of reduced metal which by mere inspection cannot be distinguished from the soot separated out on the porcelain by a smoky flame. By means of a glass rod, these films can be touched with a drop of dilute nitric acid containing about 20 per cent. of real acid; and the various degrees of solubility of the films serves as a distinguishing characteristic.

(b) *Oxide-films* are obtained by holding the porcelain basin filled with water in the *upper oxidizing flame*, the rest of the operation being the same as in the production of the metallic films. If only a very small quantity of the sample can be employed, care must be taken to lessen the size of the flame, in order that the volatile products may not be spread over too large a surface of porcelain.

The film of oxide is examined as follows:—

( $\alpha$ ) The colour of the thick and thin film is carefully observed.

( $\beta$ ) The reducing action or otherwise of a drop of stannous chloride is noted.

( $\gamma$ ) If no reduction occurs, caustic soda is added to the stannous chloride until the precipitated hydrate redissolves, and then it is to be observed whether a reduction occurs.

( $\delta$ ) A drop of perfectly neutral silver-nitrate is rubbed over the film with a glass rod, and a current of ammoniacal air is blown over the surface from a small wash-bottle containing ammonia solution, and having the mouth-tube dipping under the liquid and the exit-tube cut off close below the cork. If a precipitate is formed, the colour is observed, and the solubility or alteration, if any, noticed which occurs when the current of alkaline air is continued, or when a drop of ammonia-liquor is added.

(c) *Iodide-films* are simply obtained from the oxide-films by breathing on the latter upon the cold basin, which is then placed upon the wide-mouthed well-stoppered glass (fig. 8) containing fuming hydriodic acid and phosphorous acid derived from the gradual deliquescence of phosphoric triiodide. When the mixture no longer fumes, owing to absorption of moisture, it is easy to render it again fuming by adding a little anhydrous phosphoric acid. Other films, often containing both iodides of a metal, and therefore frequently less regular in colour and appearance, may be easily obtained by smoking the oxide-film with a flame of alcohol containing iodine in solution placed upon a bundle of asbestos-threads and held under the basin. If any iodine be condensed on the basin with the hydriodic acid, it can easily be removed by gentle warming and blowing.

The examination of the film is conducted as follows:—

( $\alpha$ ) The solubility of the film is examined simply by breathing



upon it when the basin is cooled; the colour then either changes or entirely disappears, the film being dissolved in the moisture of the breath. If the basin be gently warmed, or if it be blown upon for some distance, the film again becomes visible by the evaporation of the moisture in the current of air.

( $\beta$ ) The ammonia compound of the iodide is formed by blowing ammoniacal air upon it and noticing whether the colour of the thick and thin films alters quickly, slowly, or not at all. The different colours reappear at once if the basin be held for a few moments over an open bottle containing fuming hydrochloric acid.

( $\gamma$ ) The iodide-films generally give the same reactions as the oxide-films with silver-nitrate and ammonia, with stannous chloride, and with caustic soda.

( $d$ ) The *sulphide-film* is most easily obtained from the iodide-film by blowing upon it a current of air saturated with ammonium-sulphide, and removing the excess of sulphide by gently warming the porcelain. It is advisable to breathe on the film from time to time whilst the current of sulphuretted air is being blown on the basin. The experiments to be made with this film are:—

( $\alpha$ ) The solubility or otherwise in water is ascertained by breathing on to it, or by addition of a drop of water. The sulphides often possess the same colour as the iodide-films; they may, however, generally be distinguished by their insolubility on breathing.

( $\beta$ ) The solubility of the sulphide in ammonium-sulphide is ascertained by blowing or dropping.

4. *Films on Test-tubes*.—Under certain circumstances it is advisable not to collect the film on porcelain, but upon the outside of a large test-tube (fig. 5, *e*); this method is especially used when it is needed to collect larger quantities of the reduction film for the purposes of further examination. The fine asbestos-thread with the sample of substance is held on the glass tube (*b*) before the lamp so that it is placed at the height of the middle of the upper reducing flame, and the test-tube fixed so that the lowest point is just above the end of the asbestos-thread. If the lamp be now pushed under the test-tube, the substance and the asbestos-thread are in the reducing flame. By repeating this operation the film can be obtained of any wished-for thickness; some pieces of marble are in this case placed in the test-tube, to prevent the water from being thrown out of the tube by percussive boiling.

### III. THE REACTIONS OF THE ELEMENTS.

The elements, which can easily be recognized by their flame



reactions, are arranged in the following groups and subgroups according to their behaviour in the reducing and oxidizing flames:—

A. Elements which are reducible to metal and are deposited in films.

1. Films scarcely soluble in cold dilute nitric acid—tellurium, selenium, antimony, arsenic.
2. Films slowly and difficultly soluble in cold dilute nitric acid—bismuth, mercury, thallium.
3. Films instantly soluble in cold dilute nitric acid—cadmium, zinc, indium.

B. Elements reducible to the metallic state, giving no film.

1. Not fusible to a metallic bead.

a. Magnetic—iron, nickel, cobalt.

b. Non-magnetic—palladium, platinum, rhodium, iridium.

2. Fusible to metallic beads—copper, tin, silver, gold.

C. Elements most easily separated and recognized as compounds—tungsten, titanium, tantalum and niobium, silicon, chromium, vanadium, manganese, uranium, sulphur, phosphorus.

I now proceed to consider the special behaviour of the bodies named in the foregoing groups.

### 1. *Behaviour of the Tellurium Compounds.*

(a) *Flame-coloration*.—In the upper reducing flame pale blue, whilst the upper oxidizing flame appears green.

(b) *Volatilization* unaccompanied by any smell.

(c) *Reduction film* black, thinnest part blackish brown, dead or bright; heated with concentrated sulphuric acid gives splendid carmine-red colour.

(d) *Oxide-film* white, invisible or nearly so; stannous chloride colours it black from reduced tellurium; silver-nitrate, after blowing with ammoniacal air, yellowish white.

(e) *Iodide-film* blackish brown, thinnest part brown; disappears momentarily on breathing upon it, but not when slightly warmed; reappears on exposure to hydrochloric acid; blackened by stannous chloride.

(f) *Sulphide-film* blackish brown to black; does not disappear by breathing; soluble in sulphuretted air; reappears on warming or by dry blowing.

(g) *On the charcoal splinter with soda* yields a sodium-telluride, which, when moistened, leaves a black mark on a silver coin; and if the sample contains much tellurium, gives off a smell of telluretted hydrogen when moistened with hydrochloric acid.

2. *Behaviour of the Selenium Compounds.*

- (a) *Flame-coloration*—the bright blue of the corn-flower.
- (b) *Volatilizes* and burns, giving off the peculiar putrid smell of selenium.
- (c) *Reduction film* brick-red to cherry-red, sometimes dead, sometimes bright; heated with strong sulphuric acid, gives an olive-green solution.
- (d) *Oxide-film* white; on addition of stannous chloride, brick-red from liberated selenium; the red colour becomes darker on addition of caustic soda; silver nitrate gives a white not easily visible coloration, which disappears in a current of ammoniacal air.
- (e) *Iodide-film* brown, contains some reduced selenium, and hence cannot be completely removed either by blowing with ammoniacal air or by breathing.
- (f) *Sulphide-film* yellow to orange-red, insoluble in water, soluble in ammonium-sulphide. As the sulphide is prepared from the iodide, it also contains free selenium, and does not give very clear reactions.
- (g) *Reduction with soda on the charcoal splinter* gives sodium-selenide, producing a black mark on a silver coin when moistened, and giving rise, if the quantity be not too small, when touched with hydrochloric acid, to red selenium and a smell of seleniuretted hydrogen.

3. *Behaviour of the Antimony Compounds.*

- (a) *Flame-coloration*, by treatment in the upper reducing flame, pale green, unaccompanied by any smell.
- (b) *Reduction film* black, sometimes dead, sometimes bright.
- (c) *Oxide-film* white; moistened with perfectly neutral silver-nitrate solution and then blown on by ammoniacal air, it gives a black spot which does not disappear in ammonia. If the film be first placed over bromine-vapour the reaction cannot be obtained, owing to the oxidation of antimonious to antimonie acid. It is unaltered by stannous chloride, either with or without caustic soda.
- (d) *Iodide-film* orange-red, disappearing by breathing, and reappearing by blowing or warming: blown on with ammoniacal air it disappears, but does not return; generally it gives the same reactions as the oxide.
- (e) *Sulphide-film* orange-red; the film is difficult to blow away with sulphide of ammonium; returns on blowing with air; insoluble in water.
- (f) *With soda on charcoal splinter* gives no black stain on silver, but yields a white brittle metallic bead.

#### 4. Behaviour of the Arsenic Compounds.

(a) *Flame-coloration* in upper reducing flame pale blue, giving the well-known arsenical smell.

(b) *Reduction film* black, dead or brilliant, thin film brown.

(c) *Oxide-film* white; touched with perfectly neutral silver-nitrate and then blown with ammoniacal air, it gives a canary-yellow precipitate, soluble in ammonia. Together with the lemon-yellow precipitate, a brick-red one of silver-arsenate occurs when the film has previously been treated with bromine-vapour. Stannous chloride with and without soda produces no change.

(d) *Iodide-film* is deep yellow, disappears on breathing, but returns on drying; disappears in ammoniacal air and does not return; reappears unaltered after the action of hydrochloric acid.

(e) *Sulphide-film* lemon-yellow, disappears easily on blowing with ammonium-sulphide, and reappears on warming or blowing; insoluble in water, and does not disappear by breathing.

(f) *Reduction on charcoal splinter* yields no metallic bead.

#### 5. Behaviour of the Bismuth Compounds.

(a) *Flame-coloration* bluish, not characteristic.

(b) *Reduction film* black, dead or brilliant; thin portion of film brownish black.

(c) *Oxide-film* light yellow; unaltered by silver nitrate with or without ammonia; gives no reaction with stannous chloride, but yields black precipitate of bismuth suboxide on addition of caustic soda.

(d) *Iodide-film* is very characteristic, and remarkable for the number of tints which it assumes; the thick part is of a brown or blackish-brown colour with a shade of lavender-blue; the thin film varies from flesh-coloured to light pink; it easily disappears on breathing, and appears again on blowing; in a stream of ammoniacal air it passes from pink to orange, and on blowing or warming it again attains a chestnut-brown colour; it resembles the oxide-film in its behaviour to stannous chloride and caustic soda.

(e) *Sulphide-film* is of a burnt-umber colour, the thin parts are of a lighter coffee-brown colour; does not disappear on blowing, and is not soluble in ammonium-sulphide.

(f) *On charcoal splinter with soda* the bismuth compounds are reduced to a metallic bead, yielding, when rubbed in the mortar, bright shining yellowish splinters of metal soluble in nitric acid. The solution gives, with stannous chloride and caustic soda, black bismuth suboxide.

6. *Behaviour of the Mercury Compounds.*

(a) *Metallic film* is mouse-grey, non-coherent, and spreads over the whole basin. To obtain small traces of mercury in the reduced state, the sample is mixed with soda and saltpetre and filled into a thin test-tube 5 to 6 millims. wide and 10 to 20 millims. long. This is held by a platinum wire in the flame, whilst the bottom of the basin filled with cold water is placed close above the open end of the tube. If the quantity of mercury is considerable, the metal collects in the form of small globules which can be seen with a lens, and which can be collected into larger drops by wiping the basin with a piece of moistened filter-paper.

(b) *Oxide-film* cannot be obtained.

(c) *Iodide-film* is obtained by breathing on the metallic film and then placing it over the vessel (fig. 8) containing moist bromine. It first becomes black and then disappears, but not until after some time, as mercuric bromide is formed. If the basin be now placed above the vessel of fuming hydriodic acid, a very characteristic carmine-coloured film of mercuric iodide is produced: this is often accompanied by mercurous iodide; but neither of these disappear on breathing, nor when blown with ammoniacal air.

(d) *Sulphide-film* black, not altered by breathing or by blowing with ammonium-sulphide.

(e) *With soda on the charcoal splinter* gives no reaction.

7. *Behaviour of the Thallium Compounds.*

As the presence of a few millionths of a milligramme of thallium can be recognized by the spectroscope, it does not often happen that this metal needs to be sought for in any other way. I add the following reactions for the sake of completeness.

(a) *Flame-coloration* bright grass-green.

(b) *Metallic film* black; thin parts coffee-coloured.

(c) *Oxide-film* colourless; with stannous chloride and soda, as well as with silver-nitrate with and without ammonia, no alteration.

(d) *Iodide-film* lemon-yellow, does not disappear on breathing, or on blowing with ammoniacal air, or on addition of liquid ammonia.

(e) *Sulphide-film* formed from the oxide, black, and the thin parts bluish grey; insoluble in liquid ammonium-sulphide.

(f) *On charcoal splinter with soda* reduced to a white ductile bead, which quickly oxidizes in the air, and is acted upon by hydrochloric acid with difficulty.

In addition to the foregoing, there are two metals, viz. tin and molybdenum, which may be classed under the group A 2. These two metals, however, cannot be reduced from all their com-



pounds, and the reduction never takes place easily, owing to their slight volatility; so that it will be better to class them under the groups B 2, B 1, *b*, as they can be best distinguished by the reactions which are characteristic of these groups.

### 8. *Behaviour of the Lead Compounds.*

- (a) *They colour the flame pale blue.*
- (b) *Reduction film* black, dead or brilliant.
- (c) *Oxide-film* bright yellow-ochre-coloured; stannous chloride gives no reaction even on addition of caustic soda; silver-nitrate does not produce any reaction, either alone or on addition of ammonia.
- (d) *Iodide-film* orange- to lemon-yellow, insoluble on breathing or on moistening; disappears on blowing with ammoniacal air, and again appears on warming.
- (e) *Sulphide-film* brownish red to black; by blowing or moistening with ammonium sulphide it remains unaltered.
- (f) *On charcoal splinter with soda* gives a grey, very soft ductile metallic bead, which is slowly but completely soluble in nitric acid, yielding a white easily crystallizable salt, soluble in water, and precipitated as a white powder on addition of sulphuric acid from a capillary tube.

### 9. *Behaviour of the Cadmium Compounds.*

- (a) *Metallic film* black; the thin parts brown.
- (b) *Oxide-film* brownish black, shading off through brown to a white invisible film of suboxide, which is not altered by stannous chloride either alone or with soda; silver-nitrate produces a blackish-blue coloration of reduced metal, which is very characteristic and does not disappear on addition of ammonia.
- (c) *Iodide-film* white, no change produced by ammonia.
- (d) *Sulphide-film* lemon-yellow, insoluble in liquid ammonium.
- (e) *Reduction on charcoal splinter with soda.* The metal, owing to its volatility, can only with difficulty be obtained as a silver-white ductile bead.

### 10. *Behaviour of the Zinc Compounds.*

- (a) *Reduction film* black, in the thin parts brown.
- (b) *Oxide-film* white, and therefore invisible. To test it, a square centimetre of filter-paper moistened with nitric acid is rubbed over the surface and then rolled up on two rings of fine platinum wire, 3 millims. in diameter, and burnt. If the paper is burnt in the upper oxidizing flame at as low a temperature as possible, the ash forms a small solid mass about a square millimetre in area, which can be ignited without fusion, and becomes yellow on gently heating, appearing, however, white on cooling.

If this be moistened with a few milligrammes of a very dilute cobalt solution and ignited, it appears of a beautiful green colour on cooling. It need scarcely be added that the same reaction can be effected with the metallic film. Stannous chloride with and without soda, as well as silver-nitrate with and without ammonia, give no reaction.

(c) *Iodide-film* white, not easily recognizable either by itself or after blowing with ammoniacal air.

(d) *Sulphide-film* also white, not easily recognized either with or without blowing with ammonium-sulphide.

(e) *The reduction of the metal* cannot be accomplished, owing to the volatility of zinc.

### 11. *Behaviour of the Indium Compounds.*

Indium is most easily and surely detected by the spectroscope ; the flame reactions are given for the sake of completeness.

(a) *Flame-coloration* intense, and pure indigo-colour.

(b) *Metallic film* black, the thin parts brown, either dead or brilliant ; instantly disappears in presence of nitric acid.

(c) *Oxide-film* yellowish white, scarcely visible ; gives no reaction with stannous chloride and silver solution.

(d) *Iodide-film* also yellowish white, not visible either with or without ammonia if present in small quantities.

(e) *Sulphide-film* also yellowish white, difficult to see ; unaltered by ammonium-sulphide.

(f) *Reduction on charcoal splinter with soda* is difficult ; gives silver-white ductile globules slowly soluble in hydrochloric acid.

In the accompanying Table (p. 98 & 99) the film-reactions of the foregoing elements are clearly seen.

### 12. *Behaviour of the Iron Compounds.*

(a) *Reduction on charcoal splinter* gives no metallic bead or ductile lustrous particles ; the finely divided metal forms a black brush on the end of the magnetized knife-blade ; this, when rubbed off on paper and dissolved in a drop of aqua regia, yields a yellow spot when warmed over the flame, which, when moistened with potassium-ferrocyanide, gives a deep coloration of prussian blue. The yellow spot moistened with caustic soda and then held for a few moments in a vessel with bromine-vapour gives, on a second addition of soda, no coloration of a higher oxide.

(b) *Borax bead*.—In the oxidizing flame, when hot, yellow to brownish red ; when cold, yellow to brownish yellow ; reducing flame bottle-green.

13. *Behaviour of the Nickel Compounds.*

(a) *Reduction on charcoal splinter*.—On pulverizing the charcoal the metal obtained as white, lustrous, ductile particles, forming a brush on the magnetized blade. The metal dissolved in nitric acid on paper gives a green solution, which on moistening with soda, exposure to bromine-vapour, and subsequent addition of soda, gives a blackish-brown spot of nickel-sesquioxide. The ash of the paper, from which the excess of soda has been washed out, can be used for the borax-bead test.

(b) *Borax bead*.—Oxidizing flame greyish brown or dirty violet. Upper reducing flame grey from reduced nickel, which often collects to a spongy mass of metal, rendering the bead colourless.

14. *Behaviour of the Cobalt Compounds.*

(a) *Reduction on charcoal splinter*.—By pulverizing the charcoal, as with nickel, white ductile lustrous metallic particles are obtained which form a brush on the magnetic blade. The metal, rubbed off on to paper, gives a red solution when moistened with nitric acid; this yields a green colour on addition of hydrochloric acid and drying, which disappears again on moistening. The paper moistened with soda, brought into bromine-vapour and again moistened with soda, yields a blackish-brown spot of cobalt-sesquioxide. This reaction is plainly seen with a few tenths of a milligramme of metal. The paper can also be used, after washing out the soda and burning, for the coloration of the borax bead.

(b) *Borax bead*.—In the oxidizing flame a bright-blue bead, unaltered in the lower reducing flame. The bead, when held for some time in the most powerful upper reducing flame, becomes colourless, owing to separation of metallic cobalt: this separation takes place more rapidly in presence of the platinum-ammonium-chloride, when an alloy of nickel and platinum is formed.

15. *Palladium Compounds.*

(a) *In the oxidizing flame* these compounds, heated on a fine platinum wire with soda, yield a grey mass resembling spongy platinum; this yields silver-white lustrous particles when rubbed up in the agate mortar. These particles, washed and dried on a piece of curved glass, yield a red solution with nitric acid. A drop of mercuric cyanide added to this solution forms, when blown upon by ammoniacal air, a white precipitate soluble in excess of ammonia. After evaporation, and on boiling with aqua regia, the liquid, when evaporated to a drop, deposits a dirty-orange-yellow crystalline precipitate of the ammonium-palladium-chloride.

(b) The solution of palladium is coloured blue, green, and brown by stannous chloride, according to the quantity of the reagent added.

Table of Volatile Elements which

	Metallic film.	Oxide-film.	Oxide-film with stannous chloride.	Oxide-film with stannous chloride and soda.	Oxide-film with silver-nitrate and ammonia.
Te	Black; thin part brown.	White.	Black.	Black.	Yellowish white.
Se	Cherry-red; thin part brick-red.	White.	Brick-red.	Black.	White.
Sb	Black; thin part brown.	White.	White.	White.	Black; insoluble in ammonia.
As	Black; thin part brown.	White.	White.	White.	Lemon-yellow or reddish brown; soluble in ammonia.
Bi	Black; thin part brown.	Yellowish white.	White.	Black.	White.
Hg	Grey non-coherent thin film.				
Tl	Black; thin part brown.	White.	White.	White.	White.
Pb	Black; thin part brown.	Yellow-ochre colour.	White.	White.	White.
Cd	Black; thin part brown.	Blackish brown; thin part white.	White.	White.	White; in the thin parts turns bluish black.
Zn	Black; thin part brown.	White.	White.	White.	White.
Sn	Black; thin part brown.	Yellowish white.	White.	White.	White.



can be reduced as Films.

Iodide-film.	Iodide-film with ammonia.	Sulphide-film.	Sulphide-film with ammo- nium-sul- phide.	
Brown; disappears for a time on breathing.	Disappears altogether on blowing.	Black to black- ish brown.	Disappears for a time.	Elements whose reduction-films are scarcely dis- solved in dilute nitric acid.
Brown; does not wholly disappear on breathing.	Does not dis- appear on blowing.	Yellow to orange.	Orange, and then disap- pears for a time.	
Orange-red to yel- low; disappears on breathing.	Disappears al- together on blowing.	Orange.	Disappears for a time.	
Orange-yellow; disappears for a time on breath- ing.	Disappears al- together on blowing.	Lemon-co- loured.	Does not dis- appear.	
Bluish brown; thin parts pink; dis- appears for a time on breathing.	Pink to orange; chestnut-co- loured when blowing.	Burnt-umber- colour to coffee-co- loured.	Does not dis- appear.	Elements whose reduction-films are with diffi- culty dissolved in dilute nitric acid.
Carmine-coloured and lemon-yel- low; does not disappear on breathing.	Disappears for a time on blowing.	Black.	Does not dis- appear.	
Lemon-yellow; does not disap- pear on breath- ing.	Does not dis- appear on blowing.	Black; thin parts bluish grey.	Does not dis- appear.	
Orange-yellow to lemon-colour; does not disap- pear on breath- ing.	Disappears for a time on blowing.	Brownish red to black.	Does not dis- appear.	Elements whose reduction-films are instantly dissolved in di- lute nitric acid.
White.	White.	Lemon-co- loured.	Does not dis- appear.	
White.	White.	White.	Does not dis- appear.	
Yellowish white.	Yellowish white.	White.	Does not dis- appear.	

16. *Platinum Compounds*.

(a) In the *oxidizing flame* with soda they also yield a grey spongy mass, giving white, ductile, lustrous particles on rubbing up in a mortar. These are insoluble in either nitric or hydrochloric acid alone, but dissolve in a mixture of these acids, forming, if the platinum is pure, a light-yellow solution, which is of a darker colour if rhodium, iridium, or palladium is present. The solution does not give with mercuric cyanide and ammonia a white precipitate, but a light-yellow crystalline precipitate of platinum-ammonium-chloride.

(b) Stannous chloride colours platinum compounds yellowish brown.

17. *Iridium Compounds* are likewise reduced to metal when heated with soda in the upper reducing flame, yielding a grey non-lustrous powder which is not the least ductile. This is not only insoluble in the separate acids, but also in aqua regia.

18. *Rhodium Compounds* can be distinguished from those of iridium only by the fact that the metallic powder, insoluble in aqua regia, when fused with hydropotassic sulphate, is partially oxidized, giving a rose-coloured solution.

19. *Osmium Compounds* give, in the oxidizing flame, fumes of volatile osmic acid, possessing an acrid chlorine-like smell and attacking the eyes powerfully.

20. *Gold Compounds*.—If gold is contained only in traces mixed with large quantities of the matrix, it can only be concentrated and detected by the old gold-test\*. In other cases, however, a few tenths of a milligramme can be detected by reduction with soda on a charcoal splinter. The yellow lustrous ductile globules thus obtained can be flattened out to larger golden particles; these do not dissolve in nitric or hydrochloric acid, but are pretty easily soluble in aqua regia, yielding a light-yellow solution. If this is absorbed by a small piece of filter-paper, the purple of Cassius is obtained on moistening with stannous chloride. The solution remaining on the curved glass becomes coloured brown from separation of reduced gold on addition of ferrous sulphate, whilst the solution appears blue by transmitted light.

21. *Silver Compounds*.—If silver occurs only in traces in slags or complex ores, it can only be detected by the well-known method of cupellation†. If, however, the silver compound is not mixed with a very large amount of foreign matter, it can be detected in very minute quantities by reduction with soda on the charcoal splinter. The white ductile beads dissolve easily on

\* C. F. Plattner's *Probierkunst*, bearbeitet v. Th. Richter, 1865, p. 541.

† *Ibid.* p. 512.

warming in dilute nitric acid, and yield silver-chloride with hydrochloric acid, which can then readily be recognized by its behaviour with nitric acid and ammonia. Less than one-tenth of a milligramme of silver can thus be easily detected with certainty.

## 22. *Copper Compounds.*

(a) *On the charcoal splinter with soda* the copper compounds yield a ductile lustrous metallic bead, easily recognizable by its red copper-colour. By rubbing in the mortar, flat metallic particles are obtained, which can be readily washed, and are easily soluble in nitric acid. The blue solution, absorbed on filter-paper, yields a brown stain on addition of potassic ferrocyanide. Instead of acting upon the metal in a curved glass, it may be dissolved by moistening paper upon which it is placed with nitric acid.

(b) *With borax on platinum wire.*—Blue bead, not altered to cuprous oxide when heated in the lower reducing flame alone, but on addition of very little tin-salt, forms a reddish-brown bead. If this bead be frequently oxidized and reduced in the flame, a ruby-red transparent bead is obtained; this occurs most readily when the bead is allowed to oxidize very slowly.

## 23. *Tin Compounds.*

(a) *On the charcoal splinter* the tin compounds are easily reduced to white lustrous ductile metallic beads. The flattened particles transferred to the curved glass slowly dissolve in hydrochloric acid; and the solution, when absorbed by paper, gives a red precipitate with selenious, and a black precipitate with tellurous acid dissolved in hydrochloric. If to the solution a trace of bismuth-nitrate be added, an excess of soda gives a black precipitate of bismuthous oxide. The metal acted on by nitric acid yields a white powder of insoluble stannic acid.

(b) *A borax bead*, containing enough copper-oxide to render it faintly blue, serves as a delicate test to ascertain with certainty the presence of a trace of a tin compound, as the bead placed in the lower reducing flame, as explained above, turns reddish brown, or forms a clear ruby-red glass.

## 24. *Molybdenum Compounds.*

(a) *On a charcoal splinter with soda* molybdenum is reduced to a grey powder, but with such difficulty that its detection in this way is not to be recommended. In the same way some molybdenum compounds give in the upper reducing flame a film on porcelain which it is very difficult to obtain. Molybdenum is best detected as follows.

(b) The sample, finely pulverized with the knife on the porce-

lain plate, is mixed on the hand with soda, obtained in a pasty state by melting a crystal. The mixture is then transferred on to a spiral of fine platinum wire and fused in the flame; the liquid fused mass is then knocked off the wire and allowed to fall upon the plate, when it is digested with two or three drops of water, and the clear supernatant liquid absorbed by three or four strips of filter-paper a few millimetres in breadth.

( $\alpha$ ) One of these strips, on moistening with hydrochloric acid, does not change colour, but on addition of a drop of potassium-ferrocyanide it is coloured a reddish brown.

( $\beta$ ) If one of the strips be gradually moistened with a few milligrammes of stannous chloride, it is coloured blue either at once or on gently heating; if the tint be yellow or light brown, a few drops of soda solution must be added by a capillary tube until the blue colour appears.

( $\gamma$ ) A drop of ammonium-sulphide added to the third strip produces a brown coloration; and on addition of hydrochloric acid a brown precipitate is formed, the paper, at the circumference of the drop, often being coloured blue.

( $\delta$ ) The yellow phosphate precipitate produced by the nitric acid solution of ammonium-molybdate can also be readily obtained.

( $c$ ) The borax bead is not very characteristic; in the oxidizing flame it is colourless, and in presence of much molybdenum it becomes opaque; in the reducing flame it is dark from reduced molybdenum.

**25. Tungsten Compounds.**—The reduction of tungsten can likewise be made on the charcoal splinter with soda, but this method is not available for the detection of the metal. The tungsten compounds are therefore best examined in the mode described under molybdenum, by absorbing the liquid obtained by fusion with soda on some strips of filter-paper.

( $\alpha$ ) One strip is moistened with hydrochloric acid; it remains white, but on heating turns yellow; moistened with ferrocyanide it is unaltered.

( $\beta$ ) A second strip, touched with stannous chloride, is coloured blue in the cold or on heating.

( $\gamma$ ) A drop of ammonium-sulphide causes no precipitate either by itself or after addition of hydrochloric acid; the paper becomes, however, blue- or greenish-coloured, especially on warming.

**26. Titanium Compounds** give a colourless bead with microcosmic salt in the oxidizing flame, which turns of a pale amethystine colour in the reducing flame. On addition of ferrous sulphate the bead assumes in the reducing flame the peculiar red colour of venous blood, whilst in the oxidizing flame the light-brown colour of ferric oxide can be obtained at pleasure. The



titanium compounds form with soda a bead which at first effervesces, and when hot is colourless and transparent, but on cooling becomes opaque. If to the hot bead stannous chloride be added, and if it then be heated in the lower reducing flame, a grey mass is formed, which dissolves on heating in hydrochloric acid, yielding a pale-amethystine-coloured solution.

27 & 28. *Tantalum and Niobium Compounds* exhibit the same reactions as titanium.

### 29. *Silica Compounds.*

(a) Treated with soda in the oxidizing flame, the silicates dissolve with more or less effervescence. When treated whilst hot with stannous chloride and fused, the mass does not yield a trace of blue colour on solution in warm hydrochloric acid; and the silicates may thus be distinguished from the compounds of titanitic, tantalic, or niobic acids. The blood-red colour obtained with ferric oxide from these acids is also not yielded by silicates. Gelatinous silica separates out when the fused mass is carefully treated with water and acetic acid on the lamp-plate. Fine particles of any silicate yield, on fusion in a bead of microcosmic salt, a mass of gelatinous silica when fused, which on cooling forms a solid opaque mass swimming in the transparent bead.

### 30. *Chromium Compounds.*

(a) In the *spiral of platinum wire with soda* the chromium compounds give, when fused with repeated additions of nitre, a yellow mass, which, when pulverized on the plate and treated with water, yields a light-yellow solution. If this solution be carefully poured off from the insoluble matter and acidified with acetic acid, it turns a deep orange-colour, and yields, when absorbed on strips of paper, a yellow precipitate with lead-salts, a red precipitate with mercuric salts, and a reddish-brown precipitate with silver compounds. This solution turns green on addition of ammonium-sulphide, or on treatment on the plate with aqua regia, as likewise on addition of stannous chloride.

(b) *The borax bead* is emerald-green in the oxidizing flame, and does not undergo alteration when heated in the reducing flame.

### 31. *Vanadium Compounds.*

(a) By treating the vanadium compounds with nitre and soda in the platinum spiral, a bright yellow mass is obtained; this gives a solution which, on addition of silver-nitrate and acidification with acetic acid, yields a yellow precipitate. The fused mass gives a yellow instead of a green solution when evaporated with aqua regia, which becomes blue on addition of stannous chloride. If the mass contains much vanadium, the solution

gives a yellowish-brown colour or precipitate on addition of an excess of cold concentrated hydrochloric acid.

(b) *In the borax bead* the vanadium compounds give in the oxidizing flame a greenish yellow, in the reducing flame a green colour.

### 32. *Manganese Compounds.*

(a) These give an amethystine-coloured bead in the oxidizing, and a colourless bead in the reducing flame.

(b) A green-coloured bead is formed on cooling after fusion with soda, especially when some nitre is added; this, extracted with water, yields a green solution, which turns red on addition of acetic acid, and then often becomes colourless, with separation of brown flocculi.

### 33. *Uranium Compounds.*

(a) These give a yellow bead in the oxidizing flame, which becomes green in the reducing flame, especially on addition of stannous chloride. These colours closely resemble those of the iron compounds, but may easily be distinguished, at least if no other colouring metallic oxide is present, by the fact that the uranium bead, when incandescent, emits a bluish-green light analogous to that which the uranium compounds exhibit when fluorescing. Beads of lead-oxide, stannic acid, and a few other substances exhibit a similar phenomenon when incandescent, but they none of them yield, like the uranium compounds, a coloured bead on cooling.

(b) Heated gently on the platinum spiral with hydropotassic sulphate, the insoluble uranium compounds can be decomposed. The melted mass is powdered with a few particles of crystallized sodic carbonate, and the moistened mass is absorbed by filter-paper. A brown spot is formed by addition of a drop of ferrocyanide to the moistened paper.

34. *Phosphorus Compounds.*—The presence of phosphorus may easily be detected, even when mixed with large quantities of other substances, as follows:—

(a) The sample having been ignited, is rubbed fine on the porcelain plate, is introduced into a small glass tube of the thickness of a straw; into this tube, which is closed at the bottom, a piece of magnesium wire, about one-fourth of an inch in length, is placed so that it is covered by the powder. On heating the tube, magnesium-phosphide is formed with incandescence. The black contents of the tube powdered on the plate give, on moistening with water, the highly characteristic smell of phosphuretted hydrogen. A piece of sodium can be equally well used if magnesium cannot be procured.

(b) If it has been ascertained that the sample does not yield

any film on porcelain in the upper oxidizing flame, the phosphates may be recognized by heating on platinum with borax and a thin piece of iron wire in the hottest part of the reducing flame, when a bright molten bead of iron-phosphide is obtained which can be extracted with the magnetized knife on crushing the bead under paper.

### 35. *Sulphur Compounds.*

(a) These give a fused mass with soda on the charcoal splinter, which leaves a black stain when brought on to moistened silver. As selenium and tellurium give rise to the same reaction, the absence of these substances must first be ascertained by seeing that no film of selenium or tellurium is deposited on porcelain.

(b) In the case of metallic sulphides, and not of sulphates, the simple ignition of the sample in the flame is sufficient to produce the peculiar smell of burning sulphur.

It is impossible in a limited space to follow out the application of the foregoing methods to all the special cases of the analysis of complicated mixtures. I confine myself, therefore, to illustrating the value of those methods in one or two examples.

#### 1. *A mixture of the sulphides of arsenic, antimony, and tin.*

If in a mixture of these three sulphides, containing only traces of antimony and tin, they are separated according to the ordinary rules of qualitative analysis, by dissolving in alkaline sulphides and reprecipitation with acids, the detection of these two metals by the regular tests is extremely uncertain and troublesome. According to the following method, the detection of these metals is rendered easy and certain when the proportion of tin is only a few thousandths, and that of the antimony only a few hundredths of the total weight of the mixture.

Three decigrammes of the sulphides are roasted on a curved piece of glass, small enough to be altogether surrounded by the flame, and the residue, weighing only a few milligrammes, is scraped together with the knife. The moistened mass is then collected on the end of a thread of asbestos, and a strong metallic film obtained on the test-tube (see page 90). In order to prevent the deposition of any carbon with the metals, which would act injuriously in the subsequent operations, the upper reducing flame is made so small that the luminous point is only just visible. The film is next dissolved in a drop or two of nitric acid in the curved rim of the plate (fig. 3), and the solution evaporated below its boiling-point by gently warming and blowing, so as to obtain the solid residue in as small a space as possible.



A drop of neutral silver solution is now brought on to the residue at the moment when it becomes solid; and on blowing with ammoniacal air, a characteristic black stain is formed, whilst the reaction of arsenic is also generally noticed.

In order to detect tin, a few scarcely visible particles of the roasted sulphides are fused on to a borax bead which has been very slightly tinted with cupric oxide. If the bead is now brought into the lower reducing flame, it becomes a ruby-red colour from reduced cuprous oxide. If the oxide be present in too large a quantity, the bead can be obtained transparent by the process described under the reactions of the copper compounds. This reaction can only be obtained in the lower reducing flame of the non-luminous gas-lamp, as in the ordinary blowpipe-flame the cupric oxide is reduced to cuprous oxide without the presence of tin-salt.

2. *Black tellurium, containing tellurium, selenium, antimony, lead, gold, and sulphur.*

After the sulphur has been detected by the smell on roasting, the metallic film is obtained on a test-tube, which is then placed inside a wider and shorter tube containing a few drops of *concentrated* sulphuric acid, so that the metallic film is surrounded by the acid. If the temperature be now gradually raised, the presence of tellurium is at once ascertained by the formation of a bright carmine-colour. If the temperature be still further raised, the tellurium oxidizes, and the olive-green colour of selenium becomes visible; the cooled solution, on dilution with water, then no longer exhibits the black precipitate of tellurium, but is coloured yellowish red from the selenium. If this substance be present only in small traces, it can be best detected by looking down the length of the test-tube upon a sheet of white paper. As the common commercial sulphuric acid not unfrequently contains traces of selenium, it is well to make a blind experiment to assure one's self of its absence. The antimony is detected exactly as described in the preceding example. To detect the lead and gold, a sample is reduced on the charcoal splinter, the beads of the alloy are washed into a curved glass, and the flattened and dried metallic particles treated with pretty strong nitric acid as long as anything dissolves. The acid is then evaporated off, and the soluble portion of the residue dissolved in a drop or two of water. The solution is then brought on to a second curved glass by means of a capillary pipette, and the characteristic precipitate of lead-sulphate obtained by addition of a few milligrammes of sulphuric acid. The gold, left undissolved as a brown powder, is completely washed by frequent addition of water and removal of the same with the



capillary pipette. A portion of the dried particles of gold are fused on a charcoal splinter with soda, and yield bright golden-yellow particles in the mortar; a second portion is shown to be insoluble in hydrochloric acid, but soluble in aqua regia, and the solution after evaporation is tested with stannous chloride, and the purple of Cassius obtained. One centigramme of the substance, containing only a few tenths of a milligramme of gold, amply suffices for all these reactions.

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XIII. *On the Influence of the Tidal Wave on the Motion of the Moon.* By JAMES CROLL\*.

NEARLY twenty years ago M. Mayer showed that, as the tidal wave is always a little to the east of the moon's meridian, the attraction of the moon tends to pull back the wave against the earth's rotation. The wave thus acting as a brake or drag must diminish the motion of rotation.

The researches of Mr. Adams and M. Delaunay show that the change in the excentricity of the earth's orbit accounts for only about one-half of the secular acceleration of the moon's motion as determined by observation, namely about  $6''$  in a century. Professor Hansen suggested that the other  $6''$  would be accounted for by simply assuming that the length of the sidereal day has increased by merely  $\cdot 01197$  of a second in the course of 2000 years.

About six months ago M. Delaunay showed that the retarding effect of the tidal wave, pointed out by M. Mayer, was perfectly sufficient to account for the increase required in the length of the day. Professor W. Thomson, who has lately investigated the subject, arrives at the conclusion that in a century the earth is rotating so much slower that, regarded as a time-keeper, it is losing about four seconds in a year†.

The conclusion to which M. Delaunay has arrived is that the  $6''$  of acceleration resulting from the change in the excentricity of the earth's orbit is *real*, but that the other  $6''$  is only *apparent*‡. That is, in making our calculations regarding the actual amount of the acceleration from the date of ancient eclipses, we make it  $6''$  more than it really is, owing to our taking as a standard of measurement the present length of the sidereal day, which, on account of the influence of the tides on the earth's rotation, is now too long by a small fraction of a second.

\* Communicated by the Author.

† Phil. Mag. for June 1866 (Supplement).

‡ M. Delaunay, in his reply to M. Bertrand, has since admitted that the tides produce a *real* acceleration of the moon's motion. (*Comptes Rendus*, January 29, 1866.)

The Astronomer Royal, in an elaborate paper read before the Astronomical Society in April last, arrives at the following conclusions of an opposite character :—

(1) That the effect of friction is to accelerate the time of each individual tide.

(2) That friction does not retard the earth's rotation.

(3) That it is a further result of this friction and the consequent disturbance of the form of the waters that the moon's motion is affected; her orbit is made to become large, and her motion in longitude is retarded.

It may be stated that the latter conclusion was arrived at a year or two ago by Professor W. Thomson\*. In regard to the second conclusion, the Astronomer Royal, in a note appended to his paper, says that he has at length discovered two terms which appear to exercise a real effect on the rotation of the earth. "There is," he says, "a constant acceleration of the waters as following the moon's apparent diurnal course. As this is opposite to the direction of the earth's rotation, it follows that from the action of the moon there is a constant retarding force on the rotation of the water, and therefore (by virtue of the friction between them) a constant retarding force on the rotation of the earth's nucleus†.

In a paper published in the Philosophical Magazine for April 1864, I showed that the solar wave retards the motion of the earth around the common centre of gravity of the earth and moon in precisely the same way as the lunar wave retards the motion of the earth around the earth's centre of gravity; and that as the *vis viva* of the earth's motion around the common centre of gravity of the earth and moon is being gradually converted into heat by the friction of the solar wave and dissipated into space, the earth must therefore be continually approaching nearer to the moon. The moon being thus moving in an orbit which is gradually becoming less and less, its period of revolution must also be diminishing. Or, in other words, there is an actual acceleration of the moon's angular motion.

The reason which has prevented this important consequence from being recognized is no doubt the way in which the question is at present viewed by physicists in general. They still continue to view the influence of the wave in the way in which it first suggested itself to the mind of Mayer. They consider with him that the whole retarding effect is due to the attraction of the moon pulling the wave back to the moon's meridian against the motion of rotation. This, however, is only a part of the effect. The question must be viewed under a more general form; for it

\* Phil. Mag. for April 1864, p. 293.

† Monthly Notices of the Royal Astronomical Society, April 1866, p. 235.

is evident that the heat generated by friction in the rising of the water to form the wave before the moon's meridian is reached is as truly at the expense of the earth's rotation as the heat generated after the meridian is passed.

Suppose that in the rising of a given mass of water in the formation of the wave, a unit of heat, 1390 foot-pounds, is generated and dissipated into space before the water passes the moon's meridian. The question suggests itself, where has this 1390 foot-pounds of energy come from? The only answer that we can give is that it comes from the *vis viva* of rotation. In my former paper I showed that the rising of the water to form the wave tends to diminish the *vis viva* of rotation, and that the *vis viva* thus lost is completely restored as the water descends to its original level. But if any heat be generated during the rising and falling of the water, the *vis viva* will not be wholly restored. If, for example, 1390 foot-pounds of energy in the form of heat be generated by the friction of the water as it rises and falls, then the water on reaching its original level will owe to rotation 1390 foot-pounds of the energy borrowed as it ascended which it can never pay back. And hence the *vis viva* of rotation must be diminished by that extent.

The same result follows when mechanical work is performed by the water as it ascends or descends if heat be generated. A tide-mill, as Professor Tyndall remarks, tends to diminish the rotation of the earth.

The way in which the phenomena of the tides are usually viewed has the effect of preventing the *rationale* of the process from being clearly seen\*. Take, for example, the lunar wave. All physicists agree that it depends upon two causes, viz. the attraction of the moon, and the centrifugal force of the earth's motion around the common centre of gravity of the earth and moon. But practically, however, in explaining the phenomena the kinetic element is almost entirely overlooked, and an undue prominence is given to the static element. It is well known, for example, that students have a considerable difficulty in understanding how the water can rise on the side furthest from the moon. But no possible difficulty could be felt if the student was shown (what in theory is admitted) that the rise of the water at that place is a necessary result of the centrifugal force of the earth's motion around the common centre of gravity, that being the point furthest from the centre of rotation. By viewing the phenomena from the kinetic stand-point instead of the static, new light is cast upon the subject. We can then, as has been shown†, perceive *how* it is that heat generated by friction as the

\* Phil. Mag. for April 1864, p. 286.

† Ibid. pp. 289, 290.



water ascends and descends must tend to diminish the *vis viva* of rotation.

That the solar wave must diminish the earth's motion round the common centre of gravity of the earth and moon appears evident from the following considerations.

Suppose the diurnal rotation of the earth to be stopped, or, rather we should say, reduced to the same as that of the moon, viz. to one revolution in a month. In this case the earth would always present the same side to the moon. The lunar wave would of course exist the same as at present, only it would remain stationary on the earth's surface, seeing that the earth would always present the same side to the moon. As the water would be motionless, of course there could be no friction; no heat generated, and consequently no loss of rotation. But let us look at the influence of the solar wave. The solar wave would also, of course, exist the same as it does now, but it would move round the earth not once in twenty-four hours, as at present, but only once in a month. But however slow the water would rise and fall, a considerable amount of heat would be generated by friction. The question now arises, from what source would this energy lost in the form of heat be derived? The source would evidently be the rotation of the earth round the common centre of gravity; for it is to this source that the motion of the water is due. Suppose now the diurnal rotation of the earth to commence; new effects would certainly result, but these would not prevent the occurrence of those we are now considering. In other words, the effects which, we have seen, would take place under the above conditions, do actually at present take place. The two sets of effects do not interfere with each other. Consequently the solar wave must be slowly consuming the *vis viva* of the earth's rotation round the common centre of gravity. But it is the *vis viva* of rotation that keeps the two orbs separate from each other. Hence as this *vis viva* is being consumed, the two must be approaching nearer to each other. And this must accelerate the angular motion of the moon.

The solar wave does not consume the *vis viva* of the moon's motion around the common centre. It only consumes the earth's motion around that centre. The motion of the earth is retarded, but not the motion of the moon. Now, since the earth is gradually approaching nearer and nearer to the moon in consequence of the consumption of the centrifugal force keeping it separate from that orb, the moon must therefore be moving with all its original stock of *vis viva* in an orbit which is gradually becoming less and less. Consequently the period of its revolution must be diminishing in length.

There is still another effect which results from this condition



of things. The approach of the earth towards the moon will to a certain extent make up for the direct loss of motion due to the influence of the solar wave. But still the moon, which has sustained no loss of *vis viva*, will be moving around the common centre in a shorter period than the earth. This will therefore cause the common centre of gravity to have an exceedingly slow motion around the earth's centre of gravity. This effect may be illustrated experimentally in the following manner:—Let two balls, representing the earth and moon, connected by a rod, be made to revolve upon their common centre of gravity. Retard the motion of the ball representing the earth, and instantly the common centre of gravity (if at liberty to move) will begin to move slowly around the centre of gravity of the ball whose motion has been retarded.

It is evident, as stated on a former occasion, that the influence of the tidal wave will not only stop the diurnal motion of the earth, but will ultimately bring the moon to the earth's surface.

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#### XIV. *On the Influence of the Absorption of Heat on the Formation of Dew.* By PROFESSOR MAGNUS\*.

SINCE heat is emitted by bodies in the same proportion as that in which they absorb it, by the determination of their radiating power their absorption is given, while conversely the absorption gives the radiation. In the case of solid bodies either determination can be readily executed. With liquids the determination of radiation is attended with difficulties; for as only the surface is free, that is, covered by no solid substance, it is only the radiation in an upward direction which can be observed, in which case ascending currents exert a disturbing influence. A thin layer of liquid adhering to a solid vertical side, as in Leslie's cube, cannot be used for determining radiation; for it has not everywhere the same thickness, and seldom covers all parts of the solid side; it is moreover so thin that it transmits the rays of this side itself, so that not merely the action of the liquid alone, but also, with it, that of the solid side is observed. The difficulty of determining the radiation of gaseous bodies is still greater; for they must be used without any solid side. I have, however, made a few determinations of the radiation of dry and of moist air, and some other gases and vapours. Hitherto the capacity of these bodies to transmit heat has alone been determined, and all the heat which did not pass through has been considered to be absorbed, the bodies having been enclosed in glass tubes closed at each end by rock-salt plates. Now there is the

\* Translated from the February Number of the *Berliner Monatsberichte*.

drawback in the case of aqueous vapour, that it condenses on the rock-salt; and as even the thinnest layer of water only transmits an exceedingly small quantity of heat, the result is interfered with by that thin layer of water. To remove this drawback I quite avoided rock-salt plates, by bringing the thermopile inside a tube in a vertical position; the top part of the tube was closed by very thin glass, which was directly heated externally, and thus served as source of heat. Yet as there is complete discordance between the results which I obtained for aqueous vapour by this method and those which Professor Tyndall has obtained with the use of rock-salt plates; and as this physicist, although the influence of rock-salt plates is easily ascertained, always reverts to the statement that heat is absorbed by aqueous vapour with several thousand times greater energy than by air; and as this extraordinary absorptive capacity of vapours has, both by himself and others, already been made the basis of an explanation of several important phenomena in meteorology and in terrestrial physics, I have considered it a duty incumbent on me to compare, if possible, in another manner, the absorption of heat by aqueous vapour with that by air. For this purpose the comparison of its radiation seemed especially fitted, as all solid walls were thus avoided.

Such a comparison has been made by Professor Frankland in London\*, and described in a paper "On the Physical Cause of the Glacial Epoch." He says there that he has devised a simple method of experimentally proving the radiation of aqueous vapour so that several persons could see the effect at once. "A charcoal chauffer, 14 inches high and 6 inches in diameter, is placed about 2 feet from, and in front of, a thermo-electric pile, the radiation from the chauffer and fuel being carefully cut off from the pile by a double metallic screen. The deflection of the galvanometer due to the radiation from the ascending and heated carbonic acid being now carefully neutralized by a constant source of heat radiating upon the opposite face of the pile, a current of steam is made to ascend through an iron tube passing vertically through the chauffer. Instantly the galvanometer deflects for heat much more powerfully than it did previously to its compensation, when it was exposed to the full radiation from heated air and carbonic acid. When the current of steam is interrupted, the needle immediately returns to zero. If now a current of air be forced up the central tube instead of steam, either no deflection at all, or a slight one for cold occurs. The heat of the chauffer effectually prevents any condensation of the steam."

It is possible that the condensation of steam was avoided by the heat of the chauffer; yet this would presuppose that the

\* Phil. Mag. S. 4. vol. xxvii. p. 326, *note*.

steam still existed in the middle of the heated air. If it mixed with the air, it must, on the edge (where it came in contact with colder air), have been condensed and converted into mist. Now the question here simply is, whether there was any condensation, whether mist was present; for it has never been doubted that mist absorbs heat very well, and therefore radiates it equally well. It appeared desirable therefore to make the experiment in an altered form, and to compare the radiation of dry air with that of moist, as well as of some other gases and vapours.

For this purpose the gases or vapours whose radiation was to be determined were passed through a brass tube 15 millims. in internal diameter, and placed in a horizontal position. This was heated to redness by gas-flames. One end was bent upwards, so that the heated air ascended vertically. At a distance of 400 millims. from this ascending current of air, the thermopile with its two conical reflectors was placed. To protect this against lateral radiation, it was placed in a box which was a metre long by 0.6 metre in height and the same in breadth. The part of this box turned to the hot current of air was of polished sheet zinc. In front of this there was a double metallic screen, to cut off the heat radiated by the heated tube. In the zinc side, as well as in the screen, was an aperture 50 millims. in height by 25 millims. in breadth, the middle of which was in the prolongation of the axis of the thermopile. The bent part of the tube from which the heated air issued was 45 millims. from the side of the box, but was at such a depth below the aperture that no heat-rays could pass from it to the pile. The horizontal part of the brass tube was at an angle of  $40^\circ$  with the plane of the side of the box; thus neither the flames which served for heating, nor the products of combustion arising from them, especially the carbonic acid, could radiate against the pile, and the heated part of the tube was as far as possible from the side. In spite of this distance of the tube and of the interposed screen, the front side of the box became heated and radiated towards the pile. To neutralize the current thus occasioned, a vessel was placed in front of the other cone of the pile, in which water was kept boiling by steam being passed into it. By a screen moved by means of a screw, in a similar manner to that which Professor Tyndall used in his experiments, and Professor Frankland in the experiment mentioned, the cone was so far shaded that an equally strong current in the opposite direction was produced in all cases.

Recourse must be had to this method of compensation in those cases in which, as in this, a gradual heating of the pile is unavoidable; but it is far inferior to that of Melloni; for the action of the pile depends on the difference between its temperature



and that of the source of heat by which it is irradiated. If the latter is constant, the pile takes the less heat the warmer it is itself; but if its temperature alters, the indications are no longer comparable. The use of the method of compensation presupposes that the changes of temperature which the pile undergoes in the course of time, are small as compared with the actions to be measured.

The atmospheric air whose radiation was to be measured was pressed into the brass tube by means of a large bellows. If it was to be dry, it passed previously through a spacious vessel filled with pieces of fused chloride of calcium; and if it was to be saturated with aqueous vapour, through a flask in which was water that could be heated at pleasure. Arrangements were so made by means of stopcocks that the air could be passed at will either through the chloride of calcium or through water.

In order to be quite certain that in both cases the temperature of the emerging air, if not exactly, was approximately the same, and also in order to ascertain how high was the temperature of the radiating air, a thermometer was so introduced that its bulb was in the middle of the ascending current and in front of the middle of the aperture through which the heat radiated into the box and against the pile. This position was at a height of 60 millims. above the end of the brass tube. It indicated there a temperature of  $220^{\circ}$  to  $230^{\circ}$  C. It was then placed at a height of 180 millims. above the aperture, where it still indicated  $120^{\circ}$  to  $130^{\circ}$  C. During the experiments it was always in this latter position; in which it could neither radiate against the pile, nor hinder the ascending current. In both positions the temperature was the same whether dry or moist air passed through the tube, provided the pressure was the same under which the gas issued. In the case of the other gases, of which mention will immediately be made, the pressure in the heated tube was so regulated that the thermometer remained at the temperature  $120^{\circ}$  to  $130^{\circ}$  at a height of 180 millims.

When dry atmospheric air was blown through the heated tube, it produced an extremely slight action upon the column. The deflection of the very delicate galvanometer was about 3 millims. or parts of the scale\*. If the air had passed through the flask containing water, the deflection remained almost unchanged; it only increased by three to five divisions of the scale.

If instead of atmospheric air dry carbonic acid was passed through the ignited metal tube, the deflection of the galvanometer amounted to 100 to 120 divisions.

Ordinary coal-gas furnished almost the same deflection.

\* The galvanometer was the same as that described in Poggendorff's *Annalen*, vol. cxxiv. p. 479.



If atmospheric air was passed through the flask while the water in it was heated to from  $60^{\circ}$  to  $80^{\circ}$ , the air thus saturated with aqueous vapour produced a deflection which was irregular, and sometimes increased to 20 millims.; this was very gradual, while the deflections which carbonic acid and coal-gas produced set in at once, and rapidly increased to a maximum. It might be thought that from the flask to the heated part of the brass tube the vapours had so far been precipitated that there was here little or no vapour. But, leaving out of sight that such a cooling was impossible, because the short piece of tube from the flask to the heated tube was always very warm, the great quantity of aqueous vapour present in the radiating air could be readily shown by holding a glass plate in it, on which water was copiously deposited.

When the water in the flask boiled so violently that there was mist in the emergent air, the galvanometer produced a deflection of upwards of 100 divisions. The result was the same when no air was passed through the flask, but the water in it boiled so violently that the vapour issued from the heated tube, in which case mist was always seen. If no mist was visible, the galvanometer produced no greater deflection than twenty divisions, however much vapour the air contained. From the manner in which this comparatively small deflection occurred, from its irregularity, and the slow advance of the needle, one is tempted to conclude that this also depended on a formation of mist produced at the boundary of the ascending current, but not perceptible to the eye on account of its small quantity. As soon as the greater deflection was produced, the mists could each time be seen. They can be perceived with such certainty that always, if one observer first noticed the mist, the other at the telescope announced the motion of the galvanometer.

I imagined that by using the very ingenious arrangement which M. Toeppler has described in his paper, "*Observations by a New Optical Method*," under the name *Schlierenapparat*, the mist could be still more readily perceived; yet I soon found that this artificial arrangement has here no advantage—the more so, that a mistake as regards the occurrence of the mist was not possible.

Several of my friends also, who at different times were present at the experiments, especially MM. Dove, Du Bois-Reymond, Hofmann, Poggendorff, Quincke, and Riess, have convinced themselves that air, when saturated at ordinary temperatures with aqueous vapour, produced no greater deflection than about 3 millims., and, even when saturated at a higher temperature, nothing greater than 20 millims.; only when mist was visible was the deflection as great as with carbonic acid—that is, more than

100 millims. In addition to the above gentlemen, Dr. Kundt, whose help I have had the advantage of having in this investigation, has convinced himself of the accuracy of these statements.

From these experiments it follows that the radiation of *transparent* aqueous vapour (that is, of aqueous vapour in the *proper sense* of the term) is far smaller than that of carbonic acid or of coal-gas, and but little more than that of dry atmospheric air. Hence it follows that the *absorptive power* of air which contains, or is saturated with, *transparent* vapours, differs little from that of dry, and that it is only if air is misty (that is, contains condensed vapour) that it radiates and equally well absorbs heat.

The vapours of most other liquids are oxidized when they pass through the tube mixed with atmospheric air, or if, while heated, they pass into the air. With especial facility are the vapours of *ether* oxidized. When air passed through ether at the ordinary temperature of the room ( $15^{\circ}$  C.), on emerging from the heated tube the odour of aldehyde and of acetic ether could be at once perceived; at the same time the thermometer over the tube rose considerably, indicating a continued oxidation outside the tube. Corresponding to this heating, the deflection of the galvanometer was so great that it could be no longer observed.

When air passed through absolute *alcohol* at  $15^{\circ}$  C., the deflection of the galvanometer amounted to about 30 millims. only. Heated to its boiling-point, the deflection rose to 80 to 100 millims. Here also there was an oxidation, but, as compared with that of ether, it was but small. The thermometer also was unchanged, whether the air emerged from the tube free from vapour or saturated with aqueous vapour.

As regards temperature, the behaviour was the same in the case of the following liquids.

When air passed through *amylic alcohol*, it produced a scarcely perceptible deflection of the galvanometer. As this alcohol only boils at  $130^{\circ}$  to  $132^{\circ}$  C., but little vapour is formed on passing air through it. If, while the air passed, it was heated almost to its boiling-point, a deflection of 60 to 80 millims. ensued.

*Methylic alcohol*, which boils at  $65^{\circ}$ , produced a deflection of 60 millims. when used at  $15^{\circ}$  C.; if used at its boiling-point, the oxidation was so considerable that no observation could be made.

When the air passed through cold *acetic ether*, the deflection amounted to 30 to 50 millims. If heated to its boiling-point, it was 200 to 220 millims.

Through *boracic ether* at  $15^{\circ}$  a deflection of 30 millims. was obtained; heated to its boiling-point it was 100 to 110 millims.

It appeared superfluous to investigate a greater number of

vapours, since from their easy oxidability it was not possible to obtain certain results. From its unchangeability, carbonic acid affords a more certain criterion for judging the radiating power of vapours than all other vapours. Yet a comparison with it shows very decisively that aqueous vapour in its transparent condition has scarcely greater absorptive capacity for heat than dry atmospheric air, and hence that the absorptive capacity of both differs little from each other.

But I think these experiments were not needed. A well-known phenomenon, which depends on the radiation of heat, furnishes a more striking proof of the small absorptive capacity of aqueous vapour than all experiments in the laboratory. If aqueous vapour were in fact so good an absorbent of heat as Professor Tyndall maintains, dew could never be formed; for the aqueous vapour, which is indispensable for dew, would at the same time form a covering over the surface of the earth and prevent its radiation. But just where the atmosphere is particularly rich in water, in the tropics, is dew principally formed; and those regions would be devoid of all fertility were it not that moisture is imparted to the plants by dew. Should it be urged that the vapour absorbs heat indeed, but radiates a portion only back to the earth while the greater part goes to the higher regions of the atmosphere, this process of partial radiation would repeat itself from layer to layer, and hence the temperature in different layers must diminish with the height. This, however, is notoriously not the case in the formation of dew: the temperature merely sinks near the good radiating surface of the earth; and a few feet above, it is not lower than over a badly-radiating place which is not covered with dew. Further, a cooling would be impossible, since all layers of the atmosphere, just as they radiate away part of their heat from the earth, send another portion back to it. If aqueous vapour possessed so great an absorptive capacity as Professor Tyndall ascribes to it, extremely little of the radiating heat could reach the clouds, since the enormous layer of vapour extending to them would entirely absorb it. It would then be inexplicable that clouds prevent dew. Since Wells's memorable investigations, it is generally assumed that thermal rays reach the clouds almost undiminished, and are thence reflected back to the earth; if there were no such almost unhindered transmission through moist air, the clouds at their great distance could not hinder the radiation as does a board or any other solid body at a small distance from the earth.

The conclusions which Professor Frankland deduces for the glacial epoch from the great absorptive capacity of aqueous vapour, and Professor Tyndall for certain climatic phenomena, remain unchanged if nebulous be substituted for actual vapour.



For this it is which contributes to the maintenance of the beautiful green of the British Islands; for it moderates the burning rays of the sun, as well as prevents the great colds, which only occur with a clear sky and a copious radiation.

Quite recently Father Secchi in Rome\*, and Mr. Cooke at Cambridge in America†, have connected the occurrence of certain lines in the solar spectrum, which they have observed accompanies a high hygrometric state of the atmosphere, with the absorption of heat by aqueous vapour. Apart from the circumstance that, as shown by the above experiments, heat is extremely little absorbed by transparent aqueous vapour, the absorption of light indicated by the small quantity of dark lines which occur with moist air, compared with the luminous intensity of the whole spectrum, corresponds to by no means so great an absorption of heat as, according to Professor Tyndall, must occur. It might rather be maintained that in itself the small diminution in luminous intensity with moist but perfectly transparent air, is a confirmation that thermal rays are but little absorbed by such air.

Notwithstanding the great pains taken to ascribe to transparent aqueous vapours a great absorptive capacity for heat, it follows from the experiments adduced, and still more from the phenomena of dew, that this powerful absorption is not due to the transparent, but to nebulous vapours.

## XV. *Remarks on the Paper of Professor Magnus.*

*By* Professor TYNDALL, *F.R.S., &c.*‡

**I** SHOULD refrain for the present from making any remark upon the paper of my friend Professor Magnus, did I not fear that my silence might be misconstrued by meteorologists, and that they might be withheld, through a doubt as to their value, from prosecuting observations which I think are sure to expand the boundaries of their science.

For an abstract of the experiments and reasonings by which each successive objection which has been urged against the action of aqueous vapour on radiant heat has been met, I would refer to the second edition of my work 'On Heat,' pages 381 to 421. With the desire there manifested to get at the bottom of the difference between us, I approach the latest objections of Professor Magnus, regretting only that, being on the point of quitting London, I can do no more than jot down a few of the more

\* *Comptes Rendus*, vol. lx. p. 379.

† Proceedings of the American Academy of Arts and Sciences, vol. vii. January 1866. [Phil. Mag. May 1866, p. 337.]

‡ Communicated by the Author.



obvious reflections suggested by his own description of his experiments.

Professor Magnus now infers the absence of absorption from the absence of radiation. He employs as source of heat a stream of air which is first urged through water at the ordinary temperature, and afterwards caused to pass through a hot brass tube 15 millims. in diameter. On its emergence from the tube it radiates against a thermo-electric pile placed at a distance of 400 millimetres. When dry air was urged through the tube, the deflection was exceedingly small; when air moistened as above was employed, the deflection was scarcely augmented.

Now, in the first place, the amount of vapour taken up by air in its passage through cold water is so small, and the stream of such air employed by Professor Magnus is so thin, that the heat radiated from the vapour must be excessively minute. Supposing the vapour compressed to the density of ordinary atmospheric air, the average thickness of the radiating layer would probably be less than  $\frac{1}{300}$  of an inch. Even assuming the rays from this source to reach the pile without impediment, its action would be inconsiderable, if not insensible.

But the rays were not permitted to reach the pile without impediment. I assume that Professor Magnus did not deem it necessary to dry the air intervening between his source and his pile; otherwise he would have mentioned a precaution of such importance. Here, then, we have the vapour of a column of air 15 millims. thick radiating through the vapour of a layer of air 400 millims. thick, that is to say, through twenty-seven times its own thickness of a substance intensely opaque to the radiation. Considering, then, the feebleness of its origin and the difficulties in its way, it is not surprising that the radiation from the source chosen by Professor Magnus failed to produce any very sensible impression upon his galvanometer\*.

It must be borne in mind that, to obtain copious radiation from a substance so attenuated as aqueous vapour, a considerable length of it must be employed. An example will illustrate this. When enclosed in a tube 3 feet long, the radiation of sulphuric ether vapour, at 0.5 of an inch of pressure, exceeds that of olefiant gas at the pressure of the atmosphere. In a tube 3 inches long, on the contrary, the radiation from the gas is more than treble that from the vapour†. That carbonic acid gas excels aqueous

\* I have no means of judging the humidity of the radiating air as compared with that of the air through which it radiated. If the water employed to saturate the air were very cold, the latter might be the greater of the two.

† Heat as a Mode of Motion, 2nd edit. p. 381.

vapour, in the experiments of Professor Magnus, does not, therefore, surprise me.

I have at present no means of judging of the validity of the assumption by which Professor Magnus accounts for the effect observed when his air, instead of being passed through cold water, was urged through water at a temperature of  $60^{\circ}$  or  $80^{\circ}$  C. He here assumes precipitation, though there is none visible. By a similar assumption he explains the experiment of Professor Frankland, in which aqueous vapour was discharged along the axis of a cylinder of hot air and carbonic acid, and protected from precipitation by its gaseous envelope.

With regard to the formation of dew, the amount deposited depends on the quantity of vapour present in the air; and where that quantity is great, a small lowering of temperature will cause copious precipitation. Supposing 50, or even 70 per cent. of the terrestrial radiation to be absorbed by the aqueous vapour of the air, the uncompensated loss of the remaining 30 would still produce dew, and produce it copiously where the vapour is abundant. Attenuated as aqueous vapour is, it takes a good length of it to effect large absorption. I have already risked the opinion that at least 10 per cent. of the earth's radiation is intercepted within 10 feet of the earth's surface; but there is nothing in this opinion incompatible with the observed formation of dew. A surface circumstanced like that of the earth, and capable of sending unabsorbed 80 or 90 per cent. of its emission to a distance of 10 feet from itself, must of necessity become chilled, and must, if aqueous vapour in sufficient quantity be at hand, produce precipitation.

I should willingly leave to others the further development of this question, feeling assured that, once fairly recognized by field meteorologists, the evidence in favour of the action of aqueous vapour on solar and terrestrial radiation will soon be overwhelming. An exceedingly important instalment of this evidence was furnished by Lieut.-Colonel Strachey in the last Number of the *Philosophical Magazine*. It is especially gratifying to me to find my views substantiated by so excellent an observer and so philosophical a reasoner.

Let me say, in conclusion, that nothing less than a conviction based on years of varied labour and concentrated attention, could induce me to dissent, as I am forced to do, from so excellent a worker as Professor Magnus. Hitherto, however, our differences have only led to the shedding of light upon the subject; and as long as this is the result, such differences are not to be deprecated.

Royal Institution, July 2, 1866.

XVI. *On the Evaluation of Vanishing Fractions, with some Supplementary remarks on Newton's Rule.* By J. R. YOUNG, formerly Professor of Mathematics in Belfast College\*.

WHENEVER a fraction  $\frac{F(x)}{f(x)}$  takes the form  $\frac{0}{0}$  for some particular value  $a$  of  $x$ , we may replace it by  $\frac{F_1(x)}{f_1(x)}$ ,  $\frac{F_2(x)}{f_2(x)}$ , &c., in succession, till we arrive at a fraction in which numerator and denominator do not both vanish for  $x=a$ . And it is plain that these fractions will remain unaltered though for  $F_2(x)$ ,  $F_3(x)$ ,  $F_4(x)$ , &c., and at the same time for  $f_2(x)$ ,  $f_3(x)$ ,  $f_4(x)$ , &c. we substitute

$$\frac{F_2(x)}{2}, \quad \frac{F_3(x)}{2 \cdot 3}, \quad \frac{F_4(x)}{2 \cdot 3 \cdot 4}, \quad \&c.,$$

and

$$\frac{f_2(x)}{2}, \quad \frac{f_3(x)}{2 \cdot 3}, \quad \frac{f_4(x)}{2 \cdot 3 \cdot 4}, \quad \&c.$$

This being so, I think that whenever  $F(x)$  and  $f(x)$  are rational polynomials, it will be more systematic and at the same time more easy, to compute the value of the vanishing fraction as in the following examples, a step of the work on the left and a step on the right being taken alternately. It will be readily foreseen that, although no expressions of higher degree than the third are here taken, these being fully sufficient for the purpose of illustration, yet the higher the degree, and the larger the number  $a$ , the greater is the facility of this method of calculation as compared with that usually employed.

1.  $F(x) = x^3 - 2x^2 - x + 2$ ,  $f(x) = x^3 - 7x + 6$ : to find  $\frac{F(2)}{f(2)}$ .

$$\begin{array}{r} 1-2 \quad -1 \quad +2(2 \\ \underline{2} \quad \underline{0} \quad \underline{-2} \\ 0 \quad -1 \quad 0 \\ \underline{2} \quad \underline{-1} \\ 2 \quad 3 \end{array}$$

$$\begin{array}{r} 1 \quad 0-7 \quad +6(2 \\ \underline{2} \quad \underline{4} \quad \underline{-6} \\ 2 \quad -3 \quad 0 \\ \underline{2} \quad \underline{8} \\ 4 \quad 5 \end{array}$$

$$\therefore \frac{F_1(2)}{f_1(2)} = \frac{3}{5}.$$

\* Communicated by the Author.

$$2. F(x) = x^3 - 5x^2 + 3x + 9, f(x) = x^3 - x^2 - 21x + 45, x = 3.$$

$$\begin{array}{r} 1-5+3+9(3 \\ \quad 3-6-9 \\ \hline -2-3 \quad 0 \\ \quad 3 \quad 3 \\ \quad \hline \quad 1 \quad 0 \\ \quad 3 \\ \quad \hline \quad 4 \end{array} \qquad \begin{array}{r} 1-1-21+45(3 \\ \quad 3 \quad 6-45 \\ \hline 2-15 \quad 0 \\ \quad 3 \quad 15 \\ \quad \hline \quad 5 \quad 0 \\ \quad 3 \\ \quad \hline \quad 8 \end{array}$$

$$\therefore \frac{F_2(3)}{f_2(3)} = \frac{4}{8} = \frac{1}{2}.$$

$$3. F(x) = x^3 + 2x^2 - 4x - 8, f(x) = x^3 + 3x^2 - 4, x = -2.$$

$$\begin{array}{r} 1+2-4-8(-2 \\ \quad -2-0 \\ \hline 0-4 \\ \quad -2 \quad 4 \\ \quad \hline \quad -2 \quad 0 \\ \quad -2 \\ \quad \hline \quad -4 \end{array} \qquad \begin{array}{r} 1+3+0-4(-2 \\ \quad -2-2 \\ \hline 1-2 \\ \quad -2 \quad 2 \\ \quad \hline \quad -1 \quad 0 \\ \quad -2 \\ \quad \hline \quad -3 \end{array}$$

$$\therefore \frac{F_2(-2)}{f_2(-2)} = \frac{4}{3}.$$

When the general symbol  $x$  is under the radical sign, the usual method is to substitute  $a+h$  for  $x$ , and then to develop the terms containing  $a+h$  by the binomial theorem,  $a$  being the value of  $x$  for which the fraction becomes  $\frac{0}{0}$ . But it will frequently be more convenient and simple to proceed as in the following example.

If  $\frac{\sqrt{a+x} - \sqrt{2a}}{\sqrt{a+2x} - \sqrt{3a}}$ , which becomes  $\frac{0}{0}$  when  $x=a$ , be multiplied by  $\frac{\sqrt{a+x} + \sqrt{2a}}{\sqrt{a+2x} + \sqrt{3a}}$  (which, for  $x=a$ , is  $\sqrt{\frac{2}{3}}$ ), the resulting fraction will be  $\frac{x-a}{2(x-a)} = \frac{1}{2}$ ; hence, multiplying this by  $\sqrt{\frac{3}{2}}$ , we have  $\frac{1}{2}\sqrt{\frac{3}{2}}$  for the value of the original fraction, when  $x=a$ .

In like manner the fraction  $\frac{\sqrt{5x-1} - \sqrt{2}}{x-1}$  may be rationalized by multiplying it by  $\sqrt{5x-1} + \sqrt{2}$ , and  $\sqrt{5x-1} + 2$ ;



the result being  $\frac{5(x-1)}{x-1}$ ; hence the value of the proposed fraction for  $x=1$  is 5 divided by these factors when 1 is put for  $x$  in them also; that is, the value is  $\frac{5}{8\sqrt{2}}$ .

In my demonstration of Newton's rule, the case in which the sign of inequality in any of the criteria is replaced by the sign of equality is not adverted to; and Newton makes no mention of it. I propose here briefly to examine what inference may be drawn from this circumstance.

1. And first, let it be the *leading* triad of terms that furnishes this equality. Then if the roots of the equation be diminished or increased by that quantity which will cause the second coefficient in the transformed equation to be zero, it will follow, from the theorem established at the end of my paper in the May Number of this Journal, that the third coefficient in that transformed equation must be zero also. For, as there shown, the condition

$$2nA_nA_{n-2} - (n-1)A_{n-1}^2 = 0$$

necessitates the condition

$$2nA'_nA'_{n-2} - (n-1)A'^2_{n-1} = 0,$$

which, if  $A'_{n-1}=0$ , can have place only when also  $A'_{n-2}=0$ . Now if *all* the coefficients, after this third, in the transformed equation turn out to be zero, the roots of the primitive equation must all be *equal*, their common value being the  $n$ th part of the second coefficient (when divided by the first) taken with contrary sign. But if all the coefficients do not vanish, then, as is well known, the equation must have at least one pair of imaginary roots.

The inference, therefore, is that the equation must have either one pair of imaginary roots at least, or else that the roots must be all real and equal.

The same conclusion follows when it is the *final* triad that supplies the equality, since we may reverse all the coefficients.

2. But let it be an intermediate triad which furnishes the equality. Then by taking the derived equations in succession, we shall at length arrive at one of these in which the intermediate coefficients enter the *final* triad; and consequently, as just seen, this derived equation, if all its roots be not equal, must have at least two which are imaginary. In the latter case, two at least must occur in the primitive equation. In the former case the derived polynomial (after division by the first coefficient, if this be other than unit) will be a complete power; its three leading coefficients must therefore fulfil the condition of equality,

which it could not do unless the three corresponding coefficients of the primitive fulfilled that condition: hence in this case also the roots of the primitive must all be equal, or else two at least must be imaginary. The general inference, then, is this: whichever triad furnishes the condition of equality, the equation must have either two imaginary roots at least, or else *all* its roots must be equal. When, therefore, the equation is not a complete power, the sign  $=$ , in the application of Newton's criteria to the several triads of coefficients, is to be regarded as significant of the same thing as the sign  $>$ .

It may be observed here that we know that the equation  $m(x-a)^n=0$  will have all its roots equal to  $a$ ; and that by developing the first member by the binomial theorem, the above-mentioned condition of equality will have place throughout; and further, that when this condition has *not* place throughout all the triads, the first member of the equation cannot be the development of  $m(x-a)^n$ ,—in other words, that the roots of the equation cannot be all equal. Hence the theorem, that, if the roots are all equal, the condition of equality has place for every triad, holds conversely; that is, if the condition has place for every triad, the roots are all equal.

In no subject is greater caution needful, in dealing with the converse of established theorems, than in the Theory of Equations; for the most part they are inconvertible. It has been regarded as questionable, or "more than questionable," whether the converse of Newton's rule is true; but there ought to be no doubt at all on the matter. Equations, in any number, may be proposed, for which *not one* of Newton's criteria of imaginary roots holds, and yet of which the roots shall be *all* imaginary. To be convinced of this, it is sufficient to refer to the theorem marked (II.) at the end of my paper in the Journal for October 1865, to consider  $A_3$  as negative, and  $A_1$  as a comparatively small coefficient. From the theorem marked (I.), too, it is at once seen that if  $p$  in the cubic be negative, two roots of it may be imaginary, though Newton's rule could never make known the fact. And Newton himself was fully aware of the inconvertibility of this rule; for, when speaking of the marks by which to distinguish the entrance of positive roots from the entrance of negative roots, he says (I still refer to Raphson's translation), "And this is so where there are not more impossible roots than what are discovered by the rule preceding. For there may be more, although it seldom happens."

*Note.*—In the opening paragraph of my paper in the Journal for May last, the word "holds" should be replaced by "holds or fails:" the next following paragraph, however, sufficiently implies that this was intended.

I have justified the statement in the paragraph here alluded to by a reference to the series of limiting cubics; but the truth of it may be easily established in a direct manner without any such reference—thus:—

The group of conditions given in my paper in the Journal for August 1865 are all comprehended in the general form

$$(m+1)(n-\overline{m-1})A_{m-1}A_{m+1} > m(n-m)A_m^2, \quad . \quad . \quad (1)$$

where  $m$  is the exponent of  $x$  in the middle one of any triad of terms. That is to say, the triad itself being

$$A_{m+1}x^{m+1} + A_mx^m + A_{m-1}x^{m-1},$$

the triad derived from this is

$$(m+1)A_{m+1}x^m + mA_mx^{m-1} + (m-1)A_{m-1}x^{m-2};$$

and the principle affirmed is, that accordingly as (1) holds or fails, so will the following condition, in which this derived triad replaces the former, hold or fail, namely the condition

$$m(n-m+2)(m-1)(m+1)A_{m-1}A_{m+1} > (m-1)(n-\overline{m-1})(mA_m)^2,$$

or, expunging the factors common to both sides, the condition

$$(n-m+2)(m+1)A_{m-1}A_{m+1} > m(n-\overline{m-1})A_m^2.$$

Now it being remembered that, for the triad with which we are dealing, the degree of the equation is  $n-1$ , and not  $n$ , (as in the case of the former triad) we must put  $n-1$  for  $n$  in this last condition: the form will then be

$$((n-1)-m+2)(m+1)A_{m-1}A_{m+1} > m((n-1)-\overline{m-1})A_m^2,$$

which is the same as

$$(m+1)(n-\overline{m-1})A_{m-1}A_{m+1} > m(n-m)A_m^2,$$

and is thus identical with (1).

I may add, in conclusion, that if any number  $p$  of consecutive triads fulfil the condition of equality, then there will always be at least  $p+1$  or  $p$  imaginary roots; the former number if  $p$  be odd, and the latter if  $p$  be even.

The truth of this is readily seen. If the derived equation, of which the first member terminates with the last of these triads, be replaced by its reciprocal, we shall have  $p$  consecutive *leading* triads fulfilling the condition; and by diminishing or increasing the roots of this reciprocal equation by the number which causes the second term of the transformed equation to be zero, the next  $p$  terms will be zero also, just the same as if all the following triads in the equation fulfilled the condition of equality. And distinct sequences of this kind imply distinct groups of imaginary roots.

June 13, 1866.

XVII. *On the formation of Rosolic Acid and Rosaniline.*

By H. CARO\*.

IT has been recently shown by Wanklyn and myself†, that rosolic acid may be obtained from rosaniline by the same method as that by which phenol is derived from aniline. This observation indicates the existence of a common hydrocarbon skeleton in rosolic acid and rosaniline, and exhibits the dye-forming acid and the dye-forming base as members of the same natural family.

From this point of view it seemed that a comparison and study of the various methods of preparing these substances was calculated to throw light upon the constitution of both of them.

Rosolic acid is formed in a set of reactions‡ hardly less numerous and interesting than the variety of processes devised for the production of rosaniline. Discovered in 1834 by Runge§ in coal-tar, and obtained from the residues of the preparation of carbolic acid by treating them with lime, its beautiful rose-coloured compounds with alkalies and “appropriate mordants,” attracted the attention of this chemist, to whom we also owe the discovery of carbolic acid and aniline.

Runge considered rosolic acid to be a true colouring-matter capable of forming red pigments and lake-colours, rivalling in beauty those produced by safflower, cochineal, and madder. In fact, rosolic acid, or more correctly the rosolates, were the first remarkable colouring-matters derived from coal-tar. Curiously enough, notwithstanding its striking properties, rosolic acid was lost sight of by chemists, and even its existence doubted, until Tschelnitz|| noticed its formation during the prolonged contact of carbolic acid with lime, and, following the indications given by Runge, confirmed his observations upon this colouring-matter.

A more complete investigation was made by H. Müller¶, who found that a quantity of “crude carbolate of lime, which had been left for many months in a warm drying-closet, was entirely converted into a red substance, which on treatment with water gave a beautiful dark-red solution.”

About the same time, or a little earlier, Angus Smith\*\*

\* Communicated by the Author.

† Proc. Roy. Soc. vol. xv. p. 210.

‡ E. Kopp, *Moniteur Scientif.* vol. iv. p. 118.

§ Pogg. *Ann.* vol. xxxi. p. 76.

|| *Wien. Akad. Ber.* vol. xxxiii. 1857, p. 269.

¶ *Chem. Soc. Journ.* 1858, vol. xi.

\*\* Mem. of the Lit. and Phil. Soc. of Manchester, 1st Dec. 1857.



published an account of some researches upon a red colouring-matter which had been formed by the contact of lime with carbolic acid used in the manufacture of McDougall's disinfectants. This red colour was due to the presence of rosolates; and its artificial preparation was first attempted by passing vapour of carbolic acid over heated lime, and then more successfully by heating phenylate of sodium with peroxide of manganese. In this case large quantities of rosolate of sodium were readily obtained.

Dussart\* investigated the properties of rosolic acid, arriving at the same results as H. Müller. He moreover found that when rosolic acid is distilled with excess of lime and potash, carbolic acid is regenerated.

Jourdin† proved that rosolic acid could be easily obtained by heating a mixture of carbolic acid and oxide of mercury with caustic soda. At a temperature not exceeding 150° C., the reaction is quickly accomplished, and an abundance of pure rosolate of sodium is obtained. He mentions besides the formation of rosolic acid by treatment of carbolic acid with mercuric chloride. In this instance the elimination of a large amount of hydrochloric acid was observed.

F. Fol‡ found that "bisulphate of mercury produced with phenol a reddish-brown resinous matter, yielding with alkalies very soft red and rose colours, and by itself dyeing yellow." He further studied the action of arsenic acid upon "phenic or cresylic acid or other analogous substances," and observed the formation of a yellow colouring-matter, for which he proposed the name "xanthophenic acid," which, however, presented most of the well-marked characters of rosolic acid. Schützenberger and Sengenwald§ noticed the formation of rosolates during the heating of the substitution-products which they obtained by the action of chloride of iodine upon phenylic alcohol.

All these processes for the production of rosolic acid are processes of oxidation more or less direct. There is, however, another class of processes in which, besides an oxidation-action, there appears to be an action of a carbon-compound. To these belongs the process of Monnet||, who treated sulphophenylic acid with iodide of amyle at 130° C., and obtained a yellow colouring-matter, bearing a striking resemblance to rosolic acid.

Perkin and Duppa¶ found "that, when phenic and brom-

\* *Répert. de Chim. Appl.* vol. i. p. 207.

† *Répert. de Chim. Appl.* 1861, p. 218.

‡ *Chemical News*, vol. vi. p. 85.

§ *Comptes Rendus*, vol. liv. p. 197.

|| *Bull. Mulhouse*, 1861, p. 464.

¶ *Chem. News*, 1861, p. 351.

acetic acids were heated at  $120^{\circ}\text{C}$ ., two products were formed, one possessing all the properties of rosolic acid (while the other had the character of brunolic acid).” They likewise found “that a mixture of iodine and carbolic acid, when heated with formic, acetic, butyric, and valerianic acids, produce rosolic acid or a similar substance. A mixture of iodine and carbolic acid did not give a similar result (but a black solid, containing iodine).”

In an analogous manner rosolates are formed by heating monobromophenylic acid with alcoholic potash\*.

The most interesting formation of rosolic acid, and that which has led to the practical application of this colouring-matter upon a large scale, was discovered by Kolbe and Schmitt during their researches upon the synthetical formation of salicylic acid from phenylic alcohol. In a paper “On a Red Colouring-matter from Creosote”†, Kolbe and Schmitt give a detailed account of the formation and properties of a red colouring-matter which is produced by digesting at  $140^{\circ}$ – $150^{\circ}\text{C}$ ., a mixture of 1 part oxalic acid,  $1\frac{1}{2}$  part “colourless commercial creosote,” and 2 parts concentrated sulphuric acid. The resulting product appeared to the authors “to be closely related to, if not identical with, Runge’s rosolic acid”||.

This beautiful reaction was first applied commercially by Messrs. Guynon, Marnas, and Bonnet, of Lyons, for the manufacture of rosolic acid, which was converted into the remarkable red (pæonine, coralline rouge) and blue (azuline) by the action of ammonia and of aniline respectively§. The introduction of these dyes promoted the manufacture of carbolic acid, which in this country, mainly by the endeavours of Prof. F. C. Calvert and Mr. Charles Lowe of Manchester, has now arrived at a high state of perfection.

It will be observed that in the foregoing researches there is little or no indication of the degree of purity of the phenol employed by the different experimenters. I have proposed to myself to answer the following queries:—

1. Whether, the agent being simply an oxidizing one, it is necessary to have creosylic alcohol as well as phenol?

\* Körner, *Ann. der Chem. und Pharm.* vol. xxxvii. p. 203.

† *Ann. der Chem. und Pharm.* 1861, vol. cxix. p. 169.

‡	Runge’s rosolic acid (H. Müller).		{ Kolbe and Schmitt.	Calculated for the formula $\text{C}_{20}\text{H}_{16}\text{O}_3, \text{H}_2\text{O}$
				(Wanklyn and Caro).
C ....	75.61	....	74.85	74.54
H ....	5.78	....	5.15	5.59
O ....	18.61	....	20.00	19.87
	100.00		100.00	100.00

§ *Répert. de Chim. Appl.* 1862.

2. Whether, the agent being one containing carbon of the fatty series, it is possible to get rosolic acid from phenol absolutely free from cressylic alcohol?

In carrying out my design, I was at once met by the difficulty of obtaining pure phenol. Even the best crystallized and colourless specimens of carbolic acid now to be met with in commerce contain more or less cressylic alcohol. I am therefore greatly indebted to Mr. C. Lowe, who kindly supplied me with a splendidly crystallized specimen of pure hydrated carbolic acid\*, which by simple distillation is resolved into water and into perfectly pure phenylic alcohol, which immediately solidifies in the receiver. Pure phenol has a faint vinous smell, fuses at  $42^{\circ}\text{C.}$ , and boils constantly at  $184^{\circ}\text{C.}$  (correct). It shows no tendency to deliquesce, nor to get coloured in the air.

Another specimen of phenylic alcohol was obtained by the destructive distillation of salicylate of lime (prepared from gaultheria oil). It presented the same physical characters as coal-tar (phenol). Its boiling-point was found to be  $184^{\circ}\text{C.}$  (correct), and its fusing-point  $41^{\circ}\text{C.}$ †

The mixture of phenylic and cressylic alcohols employed in the following experiments was obtained by repeated fractional distillations from the higher-boiling portions of commercial cressol. It was a colourless, highly refracting liquid of faint pleasant smell, and boiling between  $194^{\circ}\text{C.}$  and  $199^{\circ}\text{C.}$

Lastly, I prepared some cressylic alcohol by treating perfectly pure hydrochlorate of toluidine with nitrous acid, and heating the resulting and diluted solution of hydrochlorate of diazotoluol to ebullition. Under evolution of nitrogen, cressylic alcohol separated out as a heavy brown oil, largely contaminated with nitrocressylic acids. Treatment with tin and hydrochloric acid destroyed these nitro-compounds; and repeated washings and, lastly, distillation over a small piece of sodium rendered cressylic alcohol perfectly colourless.

These substances were submitted to the action of peroxide of manganese (Smith) and oxide of mercury (Jourdin) in the presence of caustic soda, likewise to the action of chloride of mercury (Jourdin), sulphate of mercury, arsenic acid (Fol), and iodine.

In every instance equal quantities of pure phenol and of the mixture of phenylic and cressylic alcohols were employed, and heated with the same weights of the aforesaid reagents under conditions precisely alike, and observing the indications given by the authors of these processes. Some of these experiments have been several times repeated with altered proportions.

\* F. C. Calvert, Chem. Soc. Journ. xviii. p. 66.

† According to determinations made by C. Schorlemmer: phenol melts at  $34^{\circ}$ – $35^{\circ}$  according to Laurent.



The result was in all cases the same. Not a trace of rosolic acid could be obtained from pure phenylic alcohol, while the formation of rosolates was most decided in the corresponding experiments with the mixture of phenylic and cressylic alcohols.

Cressylic alcohol yielded not a trace of rosolates upon treatment with arsenic acid, or with hydrated oxide of mercury and caustic soda, but the addition of phenol to it gave an immediate formation of rosolic acid under these conditions.

Thus it appears that there is a most striking analogy between the preparation of rosolic acid and rosaniline; for the latter, as is well known from the beautiful experiments of Hofmann\*, is not capable of being formed by the action of oxidizing agents either upon pure aniline or pure toluidine, but is easily obtained from a mixture of the two.

Passing now to query No. 2. Pure phenol from coal-tar and from salicylic acid was mixed with concentrated sulphuric acid and oxalic acid in the proportions recommended by Kolbe and Schmitt, and maintained at a temperature of  $160^{\circ}$  C. for  $2\frac{1}{2}$  hours. There was very little evolution of gas, and an excellent yield of rosolic acid.

Kolbe and Schmitt's process, applied to a mixture of phenol and cressol, gave much more gas, and a comparatively poor yield of rosolic acid, whilst with pure cressol there was an abundant evolution of gas, and absolutely no production of rosolic acid.

The formation of rosolic acid from pure phenol was moreover proved by repeating the experiment of Monnet. Two parts of pure phenol, one part of concentrated sulphuric acid, and two parts of iodide of amyle were heated for four hours at  $115^{\circ}$  to  $120^{\circ}$  C. There was disengagement of iodine, and formation of a notable quantity of rosolic acid.

A mixture of pure phenol with bromacetic acid, or with glacial acid and iodine, or formiates and iodine, gave rosolic acid when heated in a sealed tube, thus confirming the interesting results of Perkin and Duppa.

Iodoform acts very energetically upon pure phenol (whether prepared from coal-tar or from salicylic acid).

Iodine and hydroiodic acid are liberated, and a large quantity of rosolic acid is rapidly formed.

Pure cressylic alcohol and iodoform give not a trace of rosolic acid.

The next point to be made out, was whether pure aniline, free from toluidine, is capable of giving rosaniline on treatment with reagents containing fatty carbon. For this purpose pure aniline was prepared from indigo, from pure coal-tar benzol, and from benzoic acid benzol. These specimens had been repeatedly

\* Proc. Roy. Soc. vol. xii. pp. 645-648.



tested by heating them with iodine, mercuric chloride and arsenic acid, and gave only the minutest trace of rosaniline.

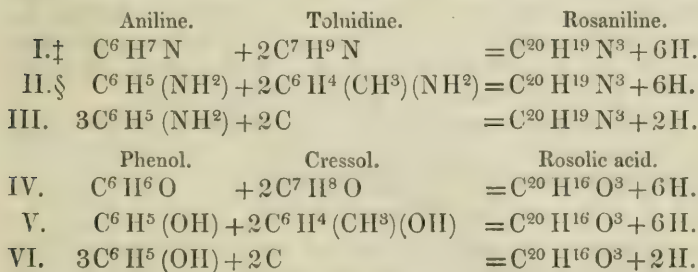
Iodoform\* was heated gently with this pure aniline. It dissolved, and almost immediately afterwards gave rise to an energetic reaction, the mixture darkening rapidly, and then solidifying from the formation of hydroiodates of aniline and rosaniline, the latter being produced in great abundance.

Under similar conditions toluidine is attacked violently, giving a brown-coloured product which contains no rosaniline.

Similar results were obtained by heating pure aniline with iodine and formiate of lead; and the formation of rosaniline was likewise, although less strikingly, observed by the action of chloroform, chloride of carbon, and iodide of cyanogen upon pure aniline.

The bearing of these experimental results on the theory of the constitution of rosolic acid and rosaniline will be obvious. Both of these substances appear to contain aromatic and fatty carbon, and accordingly we see that, in order to form either of them, it is necessary to have both a phenyle-compound and a fatty carbon-compound present. This fatty carbon-compound may be cresol or toluidine, which the researches of Tollens and Fittig† have shown to contain methyle; or it may be a simpler member of the fatty series, such as iodoform or oxalic acid.

The subjoined equations, which may be regarded as expressing the formations of rosaniline and rosolic acid, exhibit this fact, and show the very close parallelism subsisting between these formations:—



*Note.*—The fact that neither pure aniline nor pure phenol is attacked by arsenic acid or similar colour-forming re-

\* Iodoform is one of the numerous reagents patented for the production of aniline-red by Renard frères of Lyons. French patent dated December 17, 1859.

† *Ann. der Chem. und Pharm.* vol. cxxxi. p. 304.

‡ Hofmann, *Proc. Roy. Soc.* vol. xiii. p. 485.

§ Kekulé, *Ann. der Chem. und Pharm.* vol. cxxvii. p. 146.

gents, seems to corroborate these views. These agents, which are known not to act upon benzol, ammonia, or water respectively, leave the component groups of amido-benzol and hydroxyl-benzol unchanged. Thus it appears that their action consists mainly in the abstraction of hydrogen from the methyle group contained in toluidine (amido-methylbenzol) and cresol (hydroxyl-methyl-benzol), thereby increasing the atomicity of the residuary groups, and causing a coalescence of three phenyle molecules.

In the case of reagents being employed which at the same time exert an action upon, or effect a substitution in the benzol, ammonia, or water residues of aniline and phenol respectively, we can easily recognize the formation of corresponding by-products which interfere with the practical values of these processes for the formation of colouring-matters.

XVIII. *To find what changes may be made in the arrangement of the mass of a body, without altering its outward form, so as not to affect the attraction of the whole on an external point.* By Archdeacon PRATT, F.R.S.\*

1. **L**ET A represent the body in the first instance, and B after a rearrangement of the mass has taken place. Suppose each particle of B is subtracted from the correspondingly situated particle in A; we shall thus obtain an imaginary body A—B, the density of some parts being positive and of other parts negative, the whole mass being zero, and its attraction on any external point zero. Our problem amounts to finding the form and law of density of such a body. By following this process we shall discover the changes we seek for, even if they render the law of the density of the mass discontinuous.

2. The surface must evidently be a closed one. Let the origin of coordinates  $r, \theta, \omega$  be within the surface,  $\rho$  the density,  $r$  and  $a$  the general and mean radii of the surface,

$$r = a \cdot u = a(1 + u_1 + u_2 + u_3 + \dots)$$

the equation to the surface,—the first term in this series of Laplace's functions which represents  $u$  being 1, because  $a$  is the mean radius. Suppose  $\rho$  is expanded in a series of powers of  $r$ , and let

$$\rho = F + G \left( \frac{r}{a} \right) + H \left( \frac{r}{a} \right)^2 + \dots,$$

where  $F, G, H \dots$  are functions of  $\mu (= \cos \theta)$  and  $\omega$  only.

3. Let  $c$  be the distance of the attracted point from the origin,

\* Communicated by the Author.

$p$  the cosine of the angle it makes with  $r$ . Then the potential of the mass

$$= \iiint \frac{\rho r^2 d\mu d\omega dr}{\sqrt{c^2 + r^2 - 2crp}}$$

between proper limits,

$$= \int_{-1}^1 \int_0^{2\pi} \int_0^r \rho \left( \frac{r^2}{c} + \frac{r^3}{c^2} P_1 + \dots + \frac{r^{i+2}}{c^{i+1}} P_i + \dots \right) d\mu d\omega dr.$$

By the conditions this is to equal zero for all values of  $c$ . Hence it resolves itself into this,

$$\int_{-1}^1 \int_0^{2\pi} \int_0^r \rho r^{i+2} P_i d\mu d\omega dr = 0$$

for all values of  $i$  in the series  $1, 2, 3, \dots$ ,  $P_i$  being the  $i$ th Laplace's coefficient. The first term vanishes by the condition that the total mass is zero.

This last equation resolves itself into the condition that the definite integral

$$\int_0^r \rho r^{i+2} dr$$

shall be a function of  $\mu$  and  $\omega$  such that, when it is expanded into a series of Laplace's functions, the  $i$ th function shall not appear. Any other functions in the series not of the  $i$ th order will of themselves vanish when multiplied by  $P_i$  and integrated, by a known property of Laplace's functions.

4. By substituting for  $\rho$  in this last formula, integrating, and putting  $r = a \cdot u$ , we have,  $i$  being any number of the series  $1, 2, 3, \dots$  *ad infinitum*,

$$(a \cdot u)^{i+3} \left( \frac{F}{i+3} + \frac{G}{i+4} + \frac{H}{i+5} + \dots \right)$$

= some function which, when expanded into a series of Laplace's functions, has no term of the  $i$ th order. Such a function is the following:—

$$a^{i+3} (M + (i-1)M_1 + (i-2)M_2 + \dots + (i-n)M_n + \dots).$$

Equating, then, these two series and extracting the  $(i+3)$ rd root, and leaving  $u$  alone on the left side, we have

$$u = \left\{ \frac{M + (i-1)M_1 + (i-2)M_2 + \dots}{\frac{F}{i+3} + \frac{G}{i+4} + \frac{H}{i+5} + \dots} \right\}^{\frac{1}{i+3}}.$$

When the right-hand side of this is expanded into a series of

Laplace's functions ( $F, G, H \dots$  being functions of  $\mu$  and  $\omega$ , and  $M_1, M_2 \dots$  being Laplace's functions themselves), the several terms ought to be identical with the terms of the same order in  $u$  or  $1 + u_1 + u_2 + \dots$ . But, from the manner in which  $i$  enters into the second side, it is clear that every term in the series into which the second side is expanded will involve  $i$ . But  $i$  does not enter at all into the terms  $1, u_1, u_2 \dots$

Hence we must so choose our arbitrary quantities as to prevent this contradictory result. The only method of doing this is to make  $M_1=0, M_2=0, \dots$ , also to make  $F, G, H \dots$  constants, and

$$M = \frac{F}{i+3} + \frac{G}{i+4} + \frac{H}{i+5} + \dots$$

Hence  $u=1$ , and  $r=a$ ; that is, the only surface which suits the conditions is the sphere; and the law of density such that it is a function solely of the distance from the centre, since  $F, G, H \dots$  are independent of  $\mu$  and  $\omega$ .

5. This property of the sphere was of course known before, because a uniform spherical shell attracts an external point as if condensed into its own centre. But the present investigation shows that there is no other kind of surface which possesses the property. Hence no changes in the arrangement of the materials of a body can be made so as to preserve the external attraction unaltered, except uniform and complete spherical concentration and dispersion of matter to or from one or more fixed centres in the body.

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6. I trust I have now vindicated the truth of the two important propositions which have been noticed recently in your Magazine, while I have at the same time taken the opportunity of correcting and improving what I had already written\*. Both these propositions—viz. (1) that if the earth's form be a spheroid of equilibrium the arrangement of the earth's mass without doubt accords with the fluid law, and (2) that Bessel's method of applying the theory of least squares admits of improvement so as to take account of local attraction at the reference-stations (which it has hitherto altogether overlooked)—bear upon the fluid theory of the earth. For it is only by geodetic means, which the second proposition seeks to improve, that it can be ascertained whether the mean figure of the earth is a spheroid of equilibrium or not, and therefore whether the first proposition represents the state of the earth's mass.

In the ocean, which covers so large a portion of the globe, we

\* See Phil. Mag. for June and July 1866.



have at once a surface of equilibrium; and the laws of hydrostatics show that it must be a spheroid. But we have no means of actually measuring the form of the ocean. Were it studded with islands so that a large part could be covered with survey-triangles, this might be remedied. In the absence of this we are obliged to confine ourselves to the continents; and by supposing them permeated by canals letting in the sea-water to any extent, calculating by means of the spirit-level how it would lie, we ascertain by laborious surveys that the canals lie very nearly on a spheroidal surface. This surface, where it comes in contact with the sea at sea-coast stations, of course coincides with the sea-surface. But whether the sea-surface as we proceed out to sea carries on the same spheroidal form, geodesy does not enable us to determine. Perhaps accurate and extensive coast-surveys, as nearly north and south as possible, would be serviceable for this end. If the sea-surface and the inland sea-level can be shown to belong to one spheroid, then the earth's mass is undoubtedly arranged according to the fluid law.

In our ignorance of the form of the ocean by direct measurement, I think the close accordance of the ellipticity obtained by pendulum experiments, many of them made at insular stations, with that found by geodetic measures, is a fact of the last importance, and in great measure compensates for the want of direct measurement: and in our ignorance from direct sources whether or not the spheroidal surface of the continents obtained by geodesy is one of equilibrium, I think that the near agreement of the ellipticity of that surface with the ellipticity obtained from the fluid theory and an assumed law of density is a strong argument in favour of its being so.

Gosulpoor, D. B.,  
June 11, 1866.

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XIX. *Researches on the Mineralogy of South America.*

By DAVID FORBES, F.R.S., &c.\*

IV.

**DOMEYKITE.**—This mineral, originally discovered in Chile† by Professor Domeyko (after whom it has been named), and there found in the copper-veins which traverse the strata pertaining to the upper oolitic period, has now been met with by the author at Corocoro in Northern Bolivia, occurring in the beds of cupriferous sandstone of Permian or Triassic age, which

\* Communicated by the Author.

† Has since been found in the copper-mines of the La'e Superior district in North America.

apparently are the representatives of the European "Kupferschiefer."

In the mine of Buen Pastor at Corocoro it is found in the form of irregular nodules imbedded in the sandstone along with metallic copper and minute grains of metallic silver: the mine itself is explored for silver as well as copper.

The nodules vary much in size, from that of a pea up to some three or four inches across, irregularly imbedded in the comparatively soft red sandstone, which in the proximity of the nodules appears deprived of its red colour, or, as it were, bleached, apparently by some deoxidating agency—a phenomenon which is also the case in such parts of the sandstone bed in which metallic copper or silver is found, and thus serves as a guide to the miner in rejecting the non-metalliferous or unaltered part of the rock.

On fracture these nodules have considerable glance, and at first sight appear to be nearly pure Domeykite; but upon closer examination they are seen to consist of an intimate mixture of that mineral with quartz grains, the metallic glance of the Domeykite obscuring the colourless particles of sand.

The specific gravity of the richest part of such nodules was found to be 4.65 at 60° F. (15°·5 C.), whilst the metallic powder obtained upon pulverizing the nodules and washing out the intermixed quartz was found to be 6.91.

An analysis was made of these metallic particles, and the results obtained showed the mineral to have the following percentage composition:—

Arsenic . . . .	28.41
Copper . . . .	71.13
Silver . . . .	0.46
	<hr/>
	100.00

Considering the equivalent of copper to be 32, and that of arsenic 75, the formula  $\text{Cu}^6\text{As}$ , as accepted for Domeykite, would by calculation require—

Arsenic . . . .	28.19
Copper . . . .	71.81
	<hr/>
	100.00

*Titaniferous Iron-sand* (Kibdelophan?).—Along the west coast of Peru at Arica, the sands which cover the barren porphyries and other rocks subordinate to the upper oolitic series contain a considerable intermixture of black particles, easily extracted from the bulk of the sand by drawing a magnet through them, to which these particles adhere.

Although they appear homogeneous to the eye, a microscopic examination shows them to be rounded irregular grains, which still retain some adherent gangue, colourless, or of a reddish-brown

or brown colour, translucent, and probably a felspathic mineral. It was impossible to get the sand quite free from this admixture; but taken as pure as possible to obtain, the specific gravity of the black mineral was found to be 4·34 at 60° F. (15°·5 C.).

The sand was not entirely decomposed by hydrochloric acid even when previously heated in a current of hydrogen, during which operation it lost in weight, and afterwards dissolved in part in hydrochloric acid, with the evolution of hydrogen gas.

The chemical examination was therefore made by fusing a known quantity in the state of fine powder along with ten times its weight of bisulphate of potash. The fused mass when quite cold was dissolved in cold distilled water, which left behind a small amount of white insoluble silica amounting to 3·32 per cent. The filtrate, much diluted with water, was acidified by a little nitric acid, with the intention of retaining all iron in solution, when, after prolonged boiling, it deposited a considerable amount of faint yellow-coloured titanous acid, which, however, became brown upon ignition, evidently from still retaining some sesquioxide of iron. This titanous acid amounted to 57·72 per cent. of the mineral's original weight. Approximatively, therefore, the mineral may be regarded as being composed of—

Titanous acid (with some $\text{Fe}^2\text{O}^3$ )	57·72
Oxides of iron . . . . .	38·96
Insoluble silica . . . . .	3·32
	<hr/> 100·00

From which it would appear that the mineral belongs to the variety of titanoferrite called by Von Kobell "*Kibdelophan*." The analysis of the original *kibdelophan* from Gastein afforded that chemist\*—

Titanous acid . . . . .	59·00
Protoxide of iron . . . . .	36·00
Sesquioxide of iron . . . . .	4·25
Protoxide of manganese . . .	1·65
	<hr/> 100·90

whilst its specific gravity was found to be 4·661.

*Epsomite*.—This mineral is said to occur in very large quantity in the mountains near Hilo, south of Arequipa in Peru, and is sent into the interior of Peru and Bolivia, where it is employed medicinally†. It is stated to occur in veins; but in what formation is at present unknown, though it may be presumed to be a product of the volcanic action which is common to the whole of that district.

\* Schweigger-Seidel's *Journ. für Chemie und Physik*, vol. lxiv. p. 245.

† I have to thank M. Falkenheimer of La Paz for extremely large and fine specimens of this mineral.

The Epsomite presents itself in elongated masses, consisting of an aggregate of crystalline fibres, either colourless or of a white colour; streak white; hardness 1·75, scratching talc, but not rock-salt, and apparently but little less hard than the last-named substance. Lustre semivitreous to vitreous, occasionally earthy. The specific gravity was taken by weighing the mineral in petroleum at 60° F. (15°·5 C.), and calculated to be 1·636, water being 1·000.

It was readily soluble in water, leaving only a minute residue of white quartz sand; and the qualitative examination showed the absence of lime, alumina, and iron, but the presence of sulphuric acid, water, magnesia, and soda.

The quantitative analysis was conducted as follows. 23·27 grains dissolved in water left, upon filtration, a minute insoluble residue of quartz particles weighing 0·08 grain, or equivalent to 0·34 per cent. The filtrate was precipitated by a solution of chloride of barium, and afforded a precipitate of sulphate of barytes amounting to 22·26 grains, equivalent to 7·62 grains anhydrous sulphuric acid, or 32·86 per cent.

Another portion, 27·35 grains in weight, was dissolved in water and precipitated by adding acetate of barytes in slight excess. The precipitate formed was, after standing for some time, removed by filtration, and the clear solution evaporated to dryness in a platinum capsule, and heated to redness in order to convert the acetates into carbonates. The incinerated mass was then extracted with water and evaporated to dryness in a tared platinum crucible with the addition of a few drops of pure sulphuric acid. The sulphate of soda thus obtained weighed 0·21 grain, or equivalent to 0·09 grain soda, or 0·33 per cent. soda in the mineral.

In order to determine the amount of water, a third quantity, amounting to 30·06 grains, was heated in a Rammelsberg's air-bath to 300° F. (150° C.), when it sustained a loss of 12·37 grains; upon heating further to 600° F. (317° C.) more water was evolved, and this heat was continued until traces of sulphuric acid fumes commenced to show themselves, when the amount of water driven off was found to be 15·27 grains, or equivalent to 50·79 per cent.

From the above results the following percentage composition of the mineral is deduced:—

Water . . . . .	50·79
Sulphuric acid . . . .	32·86
Magnesia . . . . .	15·87
Soda . . . . .	0·33
Silica . . . . .	0·34

100·19



closely corresponding to the formula of Epsomite,  $\text{MgO SO}^3 + 7\text{HO}$ , which by calculation requires—

Water . . . . .	51.21
Sulphuric acid . . .	32.53
Magnesia . . . . .	16.26
	<hr/> 100.00

*Nitratine*.—Notwithstanding that the exploration of nitratine or nitrate of soda has for many years formed one of the most extensive and important branches of Peruvian industry, the information published in the works of different chemists and mineralogists as to its occurrence and formation appears to be extremely vague, while at the same time singularly confused views are given as to the geographical position of the deposits themselves.

One very evident source of this confusion is due to the general use of the name Chile saltpetre in commerce; this name having arisen at the commencement of the trade in this article, from the fact of the ships in which it was exported from Peru to Europe having been chartered and freighted by the merchants of Valparaiso in Chile. The name is both misleading and entirely inappropriate, as there are no available deposits of nitrate of soda known in any part of the Chilian territory. With the exception of some more recently discovered deposits on the coast of Bolivia to the south of the river Loa, which forms the line of frontier between that country and Peru, no workable deposits of nitrate of soda are known in any part of South America beyond the limits of the province of Tarapaca, in the department of Moquegua in Peru.

These remarks will help to explain some of the statements made under this head in various mineralogical and chemical works. In Ure's 'Dictionary of Arts and Manufactures,' vol. iii. p. 726, nitrate of soda is stated to be "found native in immense quantities in Chile." In Naumann's *Mineralogie*, p. 216, it is described as occurring "in Thonlagern bei Iquique und Tarapaca im Department Arequipa in Bolivia"\*. In Brooke and Miller's 'Mineralogy,' p. 61, the localities given are "Desert of Atacama," and "Tarapaca in Peru near the frontier of Chile." Again, in Burat's *Minéralogie appliqué*, p. 243, the locality is given as "principalement aux environs d'Arica et d'Iquique sur les côtes de Pérou et de la Bolivie." Both Iquique and Arica are ports on the Peruvian coast; but notwithstanding some searches were a few years back made for nitrate of soda on the coast near Arica, no nitrate of soda has ever been found anywhere near that town.

\* It must be remembered that Iquique is the chief town of the province of Tarapaca in the department of Moquegua, Peru, and that Arica is the name of a city and department in Peru still further north.

In Watts's recent and excellent 'Dictionary of Chemistry,' vol. iv. p. 105, the locality is given as "Tarapaca, Northern Chile," which also is the case in Dana's *Mineralogie*, p. 434; and both the last-mentioned authors give an analysis of *Chilian* nitratine by Hochstetter\*. Besides this analysis, all the works above referred to cite analyses of nitratine by Hayes and Lecanu, which analyses are also given by Rammelsberg in his *Handbuch der Mineralchemie*, p. 247, but he groups them all together in respect to locality, simply stating them to be all "aus dem Distrikt Atacama in Bolivia," although it is quite certain that no one of the specimens referred to came from any part of the Bolivian desert of Atacama.

Since the author's visits to this part of the Pacific coast of South America in 1857 and 1859, the results of which are published in a report on the Geology of Bolivia and Southern Peru, communicated to the Geological Society of London, Nov. 21, 1860†, a second exploration, made in 1863, has fully confirmed his previous observations, and the views expressed in that report as to the origin of these vast deposits of nitrate of soda.

The workings for the crude nitrate of soda are opened upon the inclined grounds which ascend gently from the arid salt valleys and plains which had, as it were, been bays and indentations in the eastern coast-line of the Great Plain or Pampa de Tamarugal when that was a sea, which, at an elevation of about 3250 feet above the level of the Pacific Ocean, extends over a large portion of the Province of Tarapaca in the department of Moquegua in Peru.

These deposits are known to exist from about latitude 19° S. extending to latitude 21° 30' S., where the river Loa forms the southern boundary between the Republics of Peru and Bolivia. More recent explorations in 1860 have showed that some deposits existed also to the south of the river Loa in Bolivian territory, and were subsequently worked on a small scale, the produce being shipped from the harbour of Tocopilla on the coast of Bolivia. It is, however, stated that they were soon abandoned as unprofitable.

The range of saliferous country runs parallel to the coast, at an average elevation of from 2500 to 3500 feet above the level

\* The author has referred to the *Annalen der Chemie und Pharmacie*, vol. xlv. p. 340, for the original of this analysis, and finds it was by Hofstetter, not Hochstetter, and that the mineral is there described as "natürliches, aus Perou." As this chemist is understood never to have been in the district, and the analysis corresponds to the commercial nitratine, differing greatly from all analyses of natural nitrate, it seems most probable that the analysis in question was made upon the commercial nitrate as shipped from Iquique, and which is generally supposed to be a natural product, although in reality it has been subjected to a crude process of refining.

† Quarterly Journal of the Geological Society of London, vol. xvii.

of the Pacific Ocean; and previously to having attained this elevation, it may be supposed to have been occupied by a chain of shallow lagoons broken up by promontories and islands; and these probably had for a long period tidal communication with the main ocean, until, by the still greater upheaval of the whole country, they became isolated from the sea and dried up, leaving their original sea-bottoms covered by vast beds of salt, more or less mixed with sand, and which are productive in nitrate of soda on the slopes which now bound the present valleys and plains and encircle the hills which represent the islands, bays, and indentations of the ancient lagoons.

Most descriptions of these nitrate-of-soda deposits leave the reader under the impression that they occur like other sedimentary strata, in more or less regular layers or beds of salt, sand, clay, or gypseous marls, &c. This, however, is quite erroneous. The nitrate of soda does not represent any bed in a series, but in reality is only the representative of the outcrop of a bed of salt (with which it is always more or less contaminated), or, in other words, the bed of salt left on the bottom and sides of the ancient lagoons, after their complete desiccation, becomes, at the edge of the sloping shore or bank, more or less converted into nitrate of soda by chemical action. In the centre or lower parts of the salt-bed, nitrate is never found; at the outcrop it is generally, if not always, found in more or less quantity—sometimes almost on the surface itself, or covered by a few inches of sand, but generally concealed by the upper part of the salt-bed being still unaltered salt, and forming, as it were, a hard crust (the “*crosta*” of the miners) over the soft white impure nitrate of soda.

It has been advanced that the nitrate of soda was the product of the volcanic action developed in the higher mountains to the east of the Pampa de Tamarugal, and that it had been dissolved out and washed down into these lower valleys and plains, where it had been deposited and dried up.

All the circumstances of the locality, however, tend to reject this hypothesis; and surely in that case we ought to find the nitrate deposits in the basins or lower parts of the valleys and plains; which is never the case in reality, as such low deposits invariably consist of salt, alone or mixed with the gypseous compounds usual to dried-up sea-water, whilst the nitrate-of-soda deposits are found higher up, on the slopes of the hills which surround such basins.

A very attentive study of these deposits has quite confirmed the view as to the origin of the nitrate of soda, expressed in the report previously alluded to, and which supposes the nitrate of soda to have been formed at the margin or fringe slopes of



the tidal lagoons by the decomposition of sea-salt, effected by the agency of carbonate of lime and organic matter of all kinds, both terrestrial and marine vegetation in particular. No doubt such lagoons or swamps in a tropical climate would be surrounded by a luxuriant growth of marine and other plants of semiaquatic habits; but, independent of this, the whole country in the immediate vicinity, although now perfectly arid and without a drop of surface-water, must then have been clothed by immense and luxuriant forests. This is attested by the occurrence everywhere of enormous quantities of wood, trees with branches and roots perfect and of immense size, found all over this district (buried in the plains themselves), and apparently of the same species as now grow in the country. The wood of such is found in all states, from nearly perfect preservation to extreme decay; and it may not generally be known that for many years, at the commencement of the nitrate trade, and in parts even now, these accumulations of ancient wood formed the supply of fuel for carrying on the process of boiling out the nitrate, and that it was only much later that coal, imported from England and Chile, became the chief combustible, as might be expected, from the great demand created by the subsequent great development of the trade.

Reeds, rushes, and other vegetable matter, as well as sea-shells, are constantly met with in the deposits; and at the workings of La Noria\*, it was stated that a quantity of what appeared to be guano, had also been found imbedded in the nitrate.

A chemical examination of the nitrate of soda from the deposits at La Noria about thirty miles east of Iquique, and 3052 feet above the sea, was made with the subjoined results.

The specimen taken was picked out of a large mass of the more impure "caliche" or crude nitrate, and was pronounced to be of the finest quality, and was in most parts a transparent and colourless aggregate of crystals of small size, but evidently rhombohedral. Hardness = 1.75, being below rocksalt, but scratching talc. Its specific gravity was found by taking it in petroleum, and at 60° Fahr. (15°·5 cent.) was 2.18, water being 1.000.

A careful qualitative examination showed the presence of soda, nitric acid, chlorine, sulphuric acid, and lime, with minute traces of alumina, magnesia, and potash, but iodine could not be detected by any of the usual processes.

\* The workings of La Noria and La Carolina pertain to Mr. George Smith, of Iquique, to whom the author is much indebted for the assistance afforded him in his investigations. The development of this district, both as regards nitrate of soda and the borates of lime, is greatly indebted to Mr. Smith's labours; and his map of the saliferous district, published in Lima, is a valuable contribution to science.



The quantitative analysis was effected as follows:—

100·37 grains of the nitrate dried at  $212^{\circ}$ . “The nitrate did not contain any other than hygroscopic moisture;” it dissolved into a colourless solution in cold water, and left 0·32 grain insoluble red sand, equivalent to 0·31 per cent. The solution was divided into three portions, respectively representing 50·185, 25·092, and 25·092 grains in weight of the original mineral.

50·185 grains gave, upon addition of oxalate of ammonia, a precipitate of oxalate of lime, which, upon incineration, yielded 0·22 carbonate of lime, equivalent to 0·23 per cent. of lime, or representing 0·45 per cent. chloride of calcium.

25·092 grains gave, when precipitated by nitrate of silver, 13·69 grains chloride of silver, equivalent to 13·41 per cent. chlorine, from which, after deducting 0·22 as combined with calcium, the percentage of chloride of sodium present was calculated at 21·63.

25·09 grains, when precipitated by chloride of barium, afforded 0·42 grain sulphate of barytes, equivalent to 0·52 per cent. sulphuric acid, or 0·92 per cent. sulphate of soda.

The nitrate of soda present was estimated by loss; and the analysis will therefore stand as follows:—

Nitrate of soda . . .	76·69
Sulphate of soda . . .	0·92
Chloride of sodium . .	21·63
Chloride of calcium . .	0·45
Insoluble silica . . .	0·31
	<hr/>
	100·00

The specimen represented by the above analysis must be regarded as not only far superior to the general average of what would be regarded as native nitrate of the best quality, but must be viewed more from a mineralogical than a technical point of view.

It was, however, considered interesting also to examine the more massive nitratine for sake of comparison, and for this purpose the following analysis was made.

The specimen was taken from a virgin working about to be commenced, situated on the slope of the hill overlooking the Sal de Obispo, in the interior, to the west of the port of Pisagua, and about 30 feet higher than the salt bottom of that dry plain or former lagoon.

The nitrate of soda here cropped out to the surface, barely covered by a little sand and salt, and possessed a saccharine-white appearance veined with brownish dirty-looking streaks; the quality was pronounced fine by the experienced workmen, and the specific gravity taken in petroleum was found to be 2·21

(water being 1·000). Some insoluble rock-matter was left upon dissolving in cold water, but otherwise the solution was quite colourless and transparent.

The quantitative analysis was conducted as follows :—

114·67 grains, in water, left some reddish sand-grains, which amounted to 2·35 grains or 2·04 per cent. after filtration. The solution was divided into four parts and treated as follows :—

A quarter gave, upon treatment with chloride of barium, 10·40 grains sulphate of barytes, equivalent to 12·45 per cent. sulphuric acid.

A quarter, precipitated by nitrate of silver, gave 39·42 grains mixed chloride and iodide of silver.

A quarter, supersaturated with ammonia, afforded 0·47 grain alumina (with no trace of iron), or 1·63 per cent. alumina; the filtrate, treated with oxalate of ammonia, gave upon incineration 0·09 grain carbonate of lime, equivalent to 0·17 per cent. lime; and subsequently the addition of phosphate of ammonia to the filtrate precipitated phosphate of ammonia and magnesia, which upon incineration yielded 1·26 pyrophosphate of magnesia, representing 1·81 per cent. magnesium.

The potash-determination was effected on another portion, 18·03 grains, repeatedly heated to dryness with hydrochloric acid, to expel all nitric acid; the sulphuric acid present was then removed by an alcoholic solution of chloride of strontium, and the potash determined by bichloride of platinum as usual; the metallic platinum weighed 0·19 grain, or equivalent to 0·23 per cent. potassium.

To determine the iodine another portion, 29·84 grains, was dissolved, and after filtration precipitated by chloride of palladium; 0·08 grain metallic palladium was obtained from igniting the precipitated iodide of palladium, representing 0·19 iodine.

The amount of iodine and potassium respectively found being close upon the numbers of their combining proportions, their united weights are given in the analysis as iodide of potassium.

From the above data, the analysis when calculated will stand as below :—

Nitrate of soda . . . .	21·01
Chloride of sodium . . .	55·27
Chloride of calcium . . .	0·33
Iodide of potassium . . .	0·87
Sulphate of soda . . . .	4·74
Sulphate of alumina . . .	9·81
Sulphate of magnesia . . .	5·93
Insoluble . . . . .	2·04

100·00

XX. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 78.]

April 19.—Lieut.-General Sabine, President, in the Chair.

THE following communication was read:—

“Researches on Gun-cotton.—Memoir I. Manufacture and Composition of Gun-cotton.” By F. A. Abel, F.R.S., V.P.C.S.

A review of the researches on the production, properties, and composition of gun-cotton hitherto published, and a brief examination into the probable causes of the discrepancies exhibited between the results and conclusions of different experimenters, are followed in this paper by a criticism of the several steps in the system of manufacture of gun-cotton, as prescribed by Baron v. Lenk.

The conclusions arrived at on this subject are founded upon carefully conducted laboratory-experiments, and upon extensive manufacturing operations carried on during the last three years at the Royal Gunpowder Works, Waltham Abbey. In some of these operations v. Lenk's system of manufacture, as originally communicated to the English Government by that of Austria, was strictly followed; in others, various modifications were introduced in different stages of the manufacture—such as in the composition of the acids used, in the proportion borne by the cotton to the acids in which it remained immersed, in the duration of the treatment of cotton with the acids, and in the methods of purification to which the gun-cotton was submitted.

Exception is taken to one or two points in the general system of manufacture, and directions are indicated in which they may be advantageously modified; but the general conclusion arrived at is that, although Baron v. Lenk cannot be said to have initiated any new principle as applied to the production of gun-cotton, he has succeeded in so greatly perfecting the process of converting cotton into the most explosive form of pyroxyline or gun-cotton, and also the methods of purification, as to render a simple attention to his clear and definite regulations alone necessary to ensure the manufacture of very uniform products, which are unquestionably much more perfect in their nature than those obtained in the earlier days of the history of gun-cotton. Great stress is laid upon the fact that deviations from the prescribed process which at first sight may appear trivial (such as a slight modification in the strength of the acids used, the neglect of proper cooling-arrangements) are certain to lead to variations in the products of manufacture, affecting their explosive characters, or their permanence, or both. A considerable deviation from the normal composition, due evidently to some accidental irregularities in the course of manufacture pursued, has been exhibited occasionally by gun-cotton obtained from the manufacturing works at Hirtenberg and Stowmarket.

The composition of gun-cotton has been made the subject of a very extensive series of experiments, both analytical and synthetical. The material employed in the analytical researches consisted of ordinary products of manufacture, prepared at Waltham Abbey, and



obtained from Hirtenberg and Stowmarket. The general analytical results are as follows:—

Air-dry gun-cotton contains very uniformly about two per cent. of water, which proportion it reabsorbs rapidly from the atmosphere after desiccation. If exposed to a moist confined atmosphere, it will gradually absorb as much as six per cent. of water; but it rarely retains more than two per cent. upon re-exposure to open air.

The mineral constituents of gun-cotton vary according to the quality of the water employed in its purification. The average proportion of ash furnished by gun-cotton prepared at Waltham Abbey, where the water used is hard, amounts to one per cent. It should be observed that the process of "silicating" the gun-cotton, which is prescribed by Von Lenk, but the value of which is not admitted, has been applied at Waltham Abbey only in special experimental operations. Its use naturally adds to the mineral constituents contained in the finished products.

The proportions of matters soluble in alcohol alone, and in mixtures of alcohol and ether, were found to be remarkably uniform in products of manufacture obtained by strictly following Von Lenk's directions. In the ordinary products from Waltham Abbey, the matter extractable by alcohol amounted to between 0.75 and 1 per cent., and consisted of a yellowish nitrogenized substance possessed of acid characters, and evidently produced from matters foreign to cellulose (which are retained by cotton fibre after its purification), and the products of oxidation which escape complete removal when the gun-cotton is submitted to purification in an alkaline bath. The average proportion of matter extractable by ether and alcohol after the alcoholic treatment is from 1 to 1.5 per cent. This consists of one or more of the lower products obtained by the action of nitric acid upon cotton-wool, the existence of which was established by Hadow. The causes of the invariable production of small proportions of these substances in the ordinary manufacturing operations, and of their existence in larger quantities in exceptional instances, have been carefully examined into. Their absolute removal from specimens of gun-cotton, purified for analytical purposes, was found to be almost impossible.

The methods employed for determining the proportions of carbon, hydrogen, and nitrogen in gun-cotton, and the relative proportions of carbonic acid and nitrogen furnished by its combustion, have been very carefully tested. Four different methods of determining the carbon were employed, and forty-nine successful estimations of that element have been accomplished in a variety of products of manufacture. A number of very concordant hydrogen-determinations, and eighteen direct estimations of the volumes of nitrogen furnished by the complete oxidation of gun-cotton, have been made. The individual as well as the mean results obtained in these analytical experiments correspond much more closely to the requirements of the formula  $C_6 H_7 N_3 O_{11} = C_6 \left\{ \frac{H_7}{3 N O_2} \right\} O_6$ , *trinitro-cellulose*, or  $C_{12} H_{14} O_7 3N_2 O_5$ , *trinitric cellulose*, than to the formula recently assigned for gun-cotton by Pelouze and Maury,  $C_{24} H_{30} O_{15} 5 N_2 O_5$ .



The determinations of the comparative volumes of carbonic acid and nitrogen have furnished results closely in accordance with those of the direct determination of nitrogen.

Since the specimens of gun-cotton analyzed always retained small quantities of the products soluble in ether and alcohol, it was to be expected that the proportion of nitrogen found would be slightly below, and consequently that the carbon-results would be somewhat above, those which the chemically pure substance should furnish. The variations exhibited by the analytical results do not exceed such as are ascribable to the above cause.

A number of experiments were instituted with Hadow's method of determining the composition of gun-cotton, which consists in reducing the latter to cotton by means of potassic sulphhydride. The results show that, although the method is useful for controlling the results obtained, by determining the increase of weight which cotton sustains by treatment with nitric acid, it does not afford sufficiently definite and trustworthy data to render it applicable as a method of ascertaining the degree of perfection of manufacturing products, *i. e.* the extent of freedom of a specimen of the most explosive gun-cotton from admixture with the soluble varieties.

The treatment of cotton with nitric and sulphuric acids has been varied in many ways in laboratory experiments, with the view to examine fully into the increase in weight sustained by the former, upon its conversion into the most explosive gun-cotton, and to determine what circumstances may exert an influence upon the amount of increase,—an acid mixture of uniform strength being employed throughout the experiments (3 parts by weight of sulphuric acid of spec. grav. 1.84, and 1 part of nitric acid of spec. grav. 1.52). The results arrived at may be briefly summed up as follows:—

Finely carded and carefully purified cotton-wool will sustain an increase of weight varying between 81.8 and 82.5 upon 100 parts of cotton, if submitted for 24–48 hours to treatment with a very considerable excess (about 50 parts to 1 of cotton) of the acid mixture. Similar results may also be obtained by repeatedly treating the same sample of cotton for comparatively brief periods with fresh quantities of acid, provided this treatment be not too greatly prolonged. Lower results (somewhat above or below 78 upon 100 parts of cotton) are obtained if the cotton be submitted to treatment with a large excess of acid for only brief or for very protracted periods, or if it be left for about 24 hours in contact with a comparatively limited proportion of acid (10 or 15 to 1 of cotton). The increase of weight which 100 *parts of pure cellulose* should sustain by *complete* conversion into a substance of the formula  $C_6H_7N_4O_{11}$ , is 83.3; if converted completely into a substance of the composition  $C_{24}H_{36}O_{18}, 5N_2O_5$ , it should sustain an increase in weight of 77.78.

There is strong evidence that the differences between the highest results furnished by carefully purified cotton-wool, and the number 83.3, are to be principally ascribed to the small proportions of foreign matter still existing in the fibre at the time of its conversion.

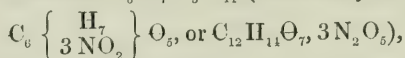
The maximum increase of weight sustained by cotton of ordinary

quality, such as is used in gun-cotton-manufacture, is, as might have been anticipated, below the result obtained, under similar conditions, with cotton of finer quality and more thoroughly purified. The highest numbers obtained by treatment of such cotton, in small quantities, with a considerable excess of acid, were somewhat below 181, from 100 of cotton. The increase of weight which this quality of cotton sustains is, however, more generally about 78 per cent.

Experiments are quoted which show that the attainment of lower results with cotton of ordinary quality is ascribable to the existence of higher proportions of foreign matters in the cotton under treatment.

Some quantitative manufacturing experiments yielded results considerably below those obtained with some of the same cotton in laboratory operations (171 and 176 of gun-cotton having been produced from 100 of cotton). The causes of these differences are investigated and explained.

The identity in their characters, and close resemblance in composition, of the most perfect results of laboratory experiments, and of the purified products of manufacture, the close approximation frequently exhibited by the weight of the former to the theoretical demands of the formula  $C_6 H_7 N_3 O_{11}$  (which may be expressed as



and the satisfactory manner in which the unavoidable production of somewhat lower results in the manufacturing operations admits of practical demonstration, appear to afford conclusive evidence of the correctness of either of the above formulæ, as representing the composition of the most explosive gun-cotton, and demonstrate satisfactorily that the material, prepared strictly according to the system of manufacture perfected by Von Lenk consists uniformly of the substance now generally known as trinitro-cellulose, in a nearly pure condition.

April 26.—J. P. Gassiot, Esq., Vice-President, in the Chair.

The following communication was read :—

“Experimental Researches in Magnetism and Electricity:”—Part I.  
By H. Wilde, Esq.

This paper is divided into two sections,—the first being on some new and paradoxical phenomena in electro-magnetic induction, and its relation to the principle of the conservation of physical force; the second on a new and powerful generator of dynamic electricity.

The author defines the principle of the conservation of force to be the definite quantitative relation existing between all phenomena whatsoever; and in the particular application of the principle to the advancement of physical science and the mechanical arts, certain problems are pointed out which, in their solution, bring out results as surprising as they are paradoxical. Although, when rightly interpreted, the results obtained are in strict accordance with the principle of conservation, yet they are, at the same time, contrary to the inferences which are generally drawn from analogical reason-

ings, and to some of those maxims which philosophers propound for the consideration of others.

The author directs attention to some new and paradoxical phenomena arising out of Faraday's important discovery of magneto-electric induction, the close consideration of which has resulted in the discovery of a means of producing dynamic electricity in quantities unattainable by any apparatus hitherto constructed. He has found that an indefinitely small amount of magnetism, or of dynamic electricity, is capable of inducing an indefinitely large amount of magnetism,—and again, that an indefinitely small amount of dynamic electricity, or of magnetism, is capable of evolving an indefinitely large amount of dynamic electricity.

The apparatus with which the experiments were made consisted of a compound hollow cylinder of brass and iron, termed by the author a magnet-cylinder, the internal diameter of which was  $1\frac{5}{8}$  inch. On this cylinder could be placed, at pleasure, one or more permanent horseshoe magnets. Each of these permanent magnets weighed about 1 lb., and would sustain a weight of about 10 lbs. An armature was made to revolve rapidly in the interior of the cylinder, in close proximity to its sides, but without touching. Around this armature 163 feet of insulated copper wire was coiled, 0.03 of an inch in diameter, and the free ends of the wire were connected with a commutator fixed upon the armature-axis, for the purpose of taking the alternating waves of electricity from the machine in one direction only. The direct current of electricity was then transmitted through the coils of a tangent galvanometer; and as each additional magnet was placed upon the magnet-cylinder, it was found that the quantity of electricity generated in the coils of the armature was very nearly in direct proportion to the number of magnets on the cylinder.

Experiments were then made for the purpose of ascertaining what relation existed between the sustaining-power of the permanent magnets of the magnet-cylinder, and that of an electro-magnet excited by the electricity derived from the armature.

When four permanent magnets capable of sustaining collectively a weight of 40 lbs. were placed upon the cylinder, and when the sub-magnet was placed in metallic contact with the poles of the electro-magnet, a weight of 178 lbs. was required to separate them. With a larger electro-magnet a weight of not less than 1080 lbs. was required to overcome the attractive force of the electro-magnet, or twenty-seven times the weight which the four permanent magnets used in exciting it were collectively able to sustain. It was further found that this great difference between the power of a permanent magnet and that of an electro-magnet excited through its agency might be indefinitely increased.

Experiments were then made with electro-magnets of various sizes, for the purpose of ascertaining the cause of these paradoxical results.

When the wires forming the polar terminals of the magneto-electric machine were connected for a short time with those of a very large electro-magnet, a bright spark could be obtained from the electro-helices twenty-five seconds after all connexion with the magneto-



electric machine had been broken. Hence it is inferred that an electro-magnet possesses the power of accumulating and retaining a charge of electricity in a manner analogous to, but not identical with, that in which it is retained in insulated submarine cables, and in the Leyden jar. It was also found that the electro-helices offered a temporary resistance to the passage of the current from the magneto-electric machine. When four magnets were placed on the cylinder, the current from the machine did not attain a permanent degree of intensity until an interval of fifteen seconds had elapsed; but when a more powerful machine was used for exciting the electro-helices, the current attained a permanent degree of intensity after an interval of four seconds had elapsed.

The general conclusion which is drawn by the author from a consideration of these experiments is, that when an electro-magnet is excited through the agency of a permanent magnet, the large amount of magnetism manifested in the electro-magnet, simultaneously with the small amount manifested in the permanent magnet, is the constant accompaniment of a correlative amount of electricity evolved from the magneto-electric machine, either all at once, in a large quantity, or by a continuous succession of small quantities,—the power which the metals (but more particularly iron) possess of accumulating and retaining a temporary charge of electricity, or of magnetism, or of both together (according to the mode in which these forces are viewed by physicists), giving rise to the paradoxical phenomena which form the subject of this part of the investigation.

Having established the fact that a large amount of magnetism can be developed in an electro-magnet by means of a permanent magnet of much smaller power, it appeared reasonable to the author to suppose that a large electro-magnet excited by means of a small magneto-electric machine could, by suitable arrangements, be made instrumental in evolving a proportionately large amount of dynamic electricity.

Two magnet-cylinders were therefore made, having a bore of  $2\frac{1}{2}$  inches, and a length of  $12\frac{1}{2}$  inches or five times the diameter of the bore.

As frequent mention is made of the different-sized machines employed in these investigations, they are distinguished by the calibre, or bore of the magnet-cylinders.

Each cylinder was fitted with an armature, round which was coiled an insulated strand of copper wire 67 feet in length, and 0.15 of an inch in diameter. Upon one of the magnet-cylinders sixteen permanent magnets were fixed, and to the sides of the other magnet-cylinder was bolted an electro-magnet formed of two rectangular pieces of boiler-plate enveloped with coils of insulated copper wire. The armatures of the  $2\frac{1}{2}$ -inch magneto-electric and electro-magnetic machines were driven simultaneously at an equal velocity of 2500 revolutions per minute. When the electricity from the magneto-electric machine was transmitted through a piece of No. 20 iron wire 0.04 of an inch in diameter, a length of 3 inches of this wire was made red-hot. When the direct current from the magneto-electric machine was transmitted through the coils of the electro-mag-



net of the electro-magnetic machine, the electricity from the latter melted 8 inches of the same-sized iron wire as was used in the preceding experiment, and a length of 24 inches was made red-hot.

When the electro-magnet of a 5-inch machine was excited by the  $2\frac{1}{2}$ -inch magneto-electric machine, the electricity from the 5-inch electro-magnetic machine melted 15 inches of No. 15 iron wire 0·075 of an inch in diameter.

The author having found that an increase in the dimensions of the machines was accompanied by a proportionate and satisfactory increase of the magnetic and electric forces, a 10-inch electro-magnetic machine was constructed: the weight of its electro-magnet is nearly 3 tons, and the total weight of the machine is about  $4\frac{1}{2}$  tons. The machine is furnished with two armatures—one for the production of “intensity”-, and the other for the production of “quantity”-effects.

The intensity armature is coiled with an insulated conductor consisting of a bundle of thirteen No. 11 copper wires, each 0·125 of an inch in diameter. The coil is 376 feet in length, and weighs 232 lbs.

The quantity armature is enveloped with the folds of an insulated copper-plate conductor 67 feet in length, the weight of which is 344 lbs. These armatures are driven at a uniform velocity of 1500 revolutions per minute, by means of a broad leather belt of the strongest description.

When the direct current from the  $1\frac{5}{8}$ -inch magneto-electric machine, having on its cylinder six permanent magnets, was transmitted through the coils of the electro-magnet of the 5-inch electro-magnetic machine, and when the direct current from the latter was simultaneously, and in like manner, transmitted through the coils of the electro-magnet of the 10-inch machine, an amount of magnetic force was developed in the large electro-magnet far exceeding anything which has hitherto been produced, accompanied by the evolution of an amount of dynamic electricity from the quantity armature so enormous as to melt pieces of cylindrical iron rod 15 inches in length, and fully one-quarter of an inch in diameter. With the same arrangement, the electricity from the quantity armature also melted 15 inches of No. 11 copper wire 0·125 of an inch in diameter.

When the intensity armature was placed in the magnet cylinder, the electricity from it melted 7 feet of No. 16 iron wire 0·065 of an inch in diameter, and made a length of 21 feet of the same wire red-hot.

The illuminating power of the electricity from the intensity armature is, as might be expected, of the most splendid description. When an electric lamp, furnished with rods of gas-carbon half an inch square, was placed at the top of a lofty building, the light evolved from it was sufficient to cast the shadows from the flames of the street-lamps a quarter of a mile distant upon the neighbouring walls. When viewed from that distance, the rays proceeding from the reflector have all the rich effulgence of sunshine.

A piece of the ordinary sensitized paper, such as is used for photographic printing, when exposed to the action of the light for twenty seconds, at a distance of 2 feet from the reflector, was darkened to the same degree as was a piece of the same sheet of paper when ex-

posed for a period of one minute to the direct rays of the sun, at noon, on a very clear day in the month of March.

The extraordinary calorific and illuminating powers of the 10-inch machine are all the more remarkable from the fact that they have their origin in six small permanent magnets, weighing only 1 lb. each, and only capable, at most, of sustaining collectively a weight of 60 lbs.; while the electricity from the magneto-electric machine employed in exciting the electro-magnet was of itself incapable of heating to redness the shortest length of iron wire of the smallest size manufactured.

The production of so large an amount of electricity was only obtained (as might have been anticipated by the physicist) by a correspondingly large amount of mechanical force; for it was found that the large electro-magnet could be excited to such a degree that the strong leather belt was scarcely able to drive the machine.

When the electro-magnet of the 10-inch machine was excited by means of the  $2\frac{1}{2}$ -inch magneto-electric machine alone, about two-thirds of the maximum amount of power from the 10-inch machine was obtained.

From a consideration of the combined action of the magneto-electric and electro-magnetic machines, the author points out a remarkable analogy, subsisting between the operation of the static forces of magnetism and of cohesion in modifying dynamical phenomena, which throws additional light upon the nature of the magnetic force.

On reviewing and comparing the whole of the analogous phenomena manifested in the operation of the magnetic and cohesive forces under the varied conditions to which the author invites attention, it appears to him that magnetism is a mode of the force of cohesion, or is, if the term be allowed, polar cohesion acting at sensible distances, the equivalent of magnetic force being obtained at the expense of an equivalent of ordinary cohesive force (in an axial direction) so long as the iron continues to be magnetized.

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#### GEOLOGICAL SOCIETY.

[Continued from vol. xxxi. p. 548.]

May 23, 1866.—Prof. A. C. Ramsay, F.R.S., Vice-President,  
in the Chair.

The following communications were read:—

1. "Notes on the Geology of Mount Sinai." By the Rev. F. W. Holland.

The physical features of the peninsula were described as exhibiting in the north an extensive tableland of limestone of Cretaceous age, supported and enclosed on the south by a long range of mountains composed of syenite, porphyries, and schistose rocks. Near Jebel Serbal is a mountain of Nummulitic limestone; and a limestone, apparently of more recent date, occurs near Tor and Ras Mohammed. The author further stated that in some parts of the peninsula the syenitic mountains are capped by horizontal beds of sandstone of considerable thickness, which are unaltered at

their contact with the syenite. This sandstone formed the great mining district of the Egyptians in Sinai, and is now worked for *turquoises*, which appear to occur more or less in veins. Raised beaches were discovered by the author, on the western side of the peninsula, at elevations of from 20 to 30 feet.

2. "On a new genus of Phyllopodous Crustacea from the Moffat Shales (Lower Silurian), Dumfriesshire." By Henry Woodward, Esq., F.G.S., F.Z.S.

The fossil described consists of the disk-shaped shield, or carapace, of an *Apus*-like Crustacean, the nearest known form to it being *Peltocaris aptychoides*, Salter, from which, however, it is at once distinguished by the absence of a dorsal furrow.

A line of suture divides the wedge-shaped rostral portion of the shield from the rest of the carapace, the two parts being seldom found together. From their strong resemblance to *Discina*, the author proposed for them the generic name *Discinocaris*, and named the species *Browniana*, after Mr. D. J. Brown, who first drew his attention to it.

3. "On the oldest known British Crab (*Protocarcinus longipes*, Bell, MS.) from the Forest Marble of Malmesbury, Wilts." By Henry Woodward, Esq., F.G.S., F.Z.S.

The author stated that three genera and twenty-five species of Brachyurous Crustacea had already been described by Prof. Reuss and H. von Meyer from the Upper White Jura of Germany; but as no limbs or abdominal segments had been met with, it was more doubtful where to place them than the species now described, which had nearly all its limbs *in situ*, and a portion of the abdomen united. *Protocarcinus* closely resembles the common spidercrabs (the *Maidæ* and *Leptopodidæ*) living on our own coasts.

4. "On the species of the genus *Eryon*, Desm., from the Lias and Oolite of England and Bavaria." By Henry Woodward, Esq., F.G.S., F.Z.S.

The genus *Eryon* of Desmarest was established for certain extremely broad and flat forms of *Astacidæ* found in the Solenhofen limestone near Munich, and first described in 1757. The late Dr. Oppel has recorded fourteen species, two of which, *E. Barrovensis* and *E. (Colcia) antiquus*, are from the Lias of England. Mr. Woodward gave descriptions and figures of *E. Barrovensis*, M'Coy, and five other species, namely, *E. crassichelis*, *E. Wilmcotensis*, and *E. Brodiei*, from the Lower Lias; *E. Moorei*, from the Upper Lias of Ilminster; and *E. Oppeli*, from the Lithographic stone of Solenhofen.

5. "Notes relating to the Discovery of Primordial Fossils in the Lingula-flags in the neighbourhood of Tyddynglwadis Silver-lead-Mine." By J. Plant, Esq., F.G.S.

The discoveries described in this paper included the finding of *Paradoxides* near the second adit of the Tyddynglwadis mine, in the Lower Lingula-beds, and subsequently of further specimens in the neighbourhood, associated with fragments of *Anoplocanus* and *Theca*. A detailed examination of the district, undertaken by the author and



Mr. E. Williamson had proved the correctness of their opinion that the strata at Tyddynglwadis belong to the Primordial zone, and that, within a limited area extending east from the boundary line of the Lower Cambrian grits, the rocks ought to yield a series of fossils of Primordial types. This examination had also enabled them to draw a section extending from the junction of the Lower and Upper Cambrians at Cefn Ddiddw to the base of Craig-y-Dinas, which was described in detail by the author, who adopted the following division of the beds:—

Lower Cambrians or Harlech Grits.		feet.
Upper Cambrians.	Lower Lingula-beds	{ Tyddynglwadis slates ..... 1,136
		{ Cwinheisian slates ..... 2,500
	Middle Lingula-beds	{ Hafod Owen sandstones... 5,000
	Upper Lingula-beds	{ Rhywffely slates ..... } 1,500
		Moel Gron slates..... }
		10,136

June 6, 1866.—Warington W. Smyth, Esq., M.A., F.R.S.,  
President, in the Chair.

The following communications were read:—

1. “On the Metamorphic and Fossiliferous Rocks of the Co. Galway.” By Prof. R. Harkness, F.R.S., F.G.S.

A great portion of the area under consideration was described as being occupied by contorted gneissose rocks, striking east and west, with a prevailing southerly dip towards the granitic area of Galway Bay. Quartzose rocks exhibiting great folds give rise to the bold mountainous scenery of Connemara; and reposing on these, and passing underneath the gneissic strata, is a band of serpentinous limestone, the structure of which is not of animal origin, but results solely from mineral association. The gneissose rocks on the north are covered unconformably by sandstones, the fossils of which indicate the horizon of the Upper Llandovery Rocks. These metamorphic rocks correspond with those of the Highlands of Scotland, representing the Upper Quartz rocks, Upper Limestone, and Upper Gneiss, the positions of which are known in consequence of the Lower Limestones at Durness having been determined to be not lower than the Llandeilo Flags.

2. “On the Metamorphic Lower Silurian Rocks of Carrick, Ayrshire.” By J. Geikie, Esq.

In surveying the southern district of Ayrshire, the author and his colleagues recognized the metamorphic character of certain Diorites, Serpentine, and crystalline felspathic rocks independently of each other; and Mr. J. Geikie had also been enabled to trace passages between the various altered rocks, which seemed to him to throw light upon the obscure process of metamorphic action. In this paper he first gave a generalized description of the metamorphic strata, dividing them into four groups—namely (1) Felspathic Rocks, (2) Diorites, (3) Serpentine, and (4) Altered Limestone and Calcareous Greywacke,—and again subdividing the Felspathic rocks into Amygdaloid, Porphyry, Brecciaform rocks, and finely crystalline Felstones, and the Serpentine into Schistose and Compact. He also described the association of serpentine with diorite,



and stated that the only igneous rocks of the district, consisting of a few dykes of felstone and greenstone, are of much later date than the metamorphism, and have not altered the strata in contact with them. These and other facts described in the paper had enabled him to arrive at the following conclusions:—(1) That the strata owe their metamorphism to hydrothermal action. (2) That the varying mineralogical character of the rocks is due principally to original differences of chemical composition, and not to infiltration of foreign matter at the time of metamorphism. (3) That the highly alkaline portions of the strata have been most susceptible of change. (4) That in beds having the same composition, but exhibiting various degrees of alteration, the intensity of the metamorphism has been in direct proportion to the amount of water present in the strata. (5) That in some places the rocks have been reduced to a pasty condition.

3. "On a *Cheirotherian Footprint* from the base of the Keuper Sandstone of Daresbury, Cheshire." By W. C. Williamson, Esq., F.R.S., Professor of Natural History, Anatomy, and Physiology in Owens College, Manchester.

The specimen in question was discovered by Mr. J. W. Kirkham, in the Lower Keuper Sandstone at Daresbury Quarry. It differs from all footprints hitherto obtained from this district, in being more quadrate, and distinctly that of a scaly animal; the separated toe is also less recurved, and approaches nearer to the other toes. The arrangement of the scales corresponds very closely with that seen in the foot of the living Alligator; many of them run across the foot in oblique lines, as is common amongst living Crocodilians, leaving no room to doubt that they represent true scales, and not irregular tubercles, such as are seen on the skin of some Batrachians. Traces of other impressions of feet occur on the slab, particularly an imperfect one with much larger and more oblong scales, especially under the heel; and this difference is so very similar to what is seen in the fore and hind feet of many Saurians, that Prof. Williamson believed that they did not belong to a Batrachian animal at all, but that they were Saurian, if not Crocodilian, in every feature.

4. "A description of some remarkable 'Heaves' or Throws in Penhalls Mine." By J. W. Pike, Esq.

This mine is situated in the parish of St. Agnes, in Cornwall, and is, from the extraordinary dislocations and heaves of the lodes and veins, without a parallel in any other part of the county. In the immediate neighbourhood of the workings, taking the well-known law that a lode or vein traversed is older than the one traversing it, there are, in the order of formation, (1) four or five tin lodes, (2) three or four "Downright" lodes, (3) innumerable "gossans," (4) a great number of slides or faults, dipping at various angles, (5) four cross courses, and (6) certain Caunting slides. The mineral productiveness of the tin-lodes is increased by the proximity of the gossans, but not by that of the slides; and although the dislocations are most perplexing to the miner, the district has yielded great riches, and has been worked from time immemorial.

XXI. *Intelligence and Miscellaneous Articles.*

ON THE COMPARATIVE VISIBILITY OF ARAGO'S, BABINET'S, AND BREWSTER'S NEUTRAL POINTS. BY MR. CHASE.

IN my communication of January 5, I stated that when Brewster's neutral point is above the horizon, I had frequently determined its position with great ease. My experience was so different from those of Brewster and Babinet, that I commenced on the 6th of March a series of comparative observations upon the three neutral points. The month which has just ended appears to warrant the following conclusions for stations in Philadelphia and its vicinity. The first, second, and sixth seem to be confirmed by observations elsewhere, while the third, fourth, and fifth, which are perhaps dependent partly upon local atmospheric peculiarities, have never, so far as I am aware, hitherto been noticed.

1. Arago's neutral point often assumes a distinctness which is never exhibited by either of the others, merely because the polarized bands in the vicinity of the sun are obscured by the dazzling brilliancy of its rays.

2. For the same reason, Babinet's neutral point is often better defined in the morning and evening than Brewster's during the middle of the day.

3. But when Brewster's and Babinet's neutral points are both above the horizon, if the sky is clear, the former is generally more easily posited than the latter. This is especially the case at midday.

4. On every clear day, and on a large portion of the days which are partially obscured by clouds, the position of each of the neutral points can be determined. Brewster records but two days during five years' observations (*Phil. Mag. S. 4. vol. xxx. p. 124*), upon which he saw all the points.

5. Arago's neutral point often rises before Brewster's sets. Under favourable atmospheric conditions the three points are, therefore, sometimes simultaneously visible.

6. Halos and clouds are frequently discernible through the polariscope which are invisible to the naked eye.

The following abstract embodies some of the results of the month's observations:—

	Days.
Satisfactory observations were made on .....	25
All the neutral points were seen on .....	17
There were no satisfactory observations on .....	6
„ 39 observations of Arago's neutral point on..	23
„ 93 „ Babinet's „ „ ..	22
„ 59 „ Brewster's „ „ ..	20
Arago's neutral point was remarkably distinct on .....	4
Babinet's „ „ „ „ .....	10
Brewster's „ „ „ „ .....	11
Arago's was the only one observed on .....	2
Babinet's „ „ „ „ .....	1
Babinet's and Brewster's the only ones seen on .....	1
Arago's and Babinet's „ „ „ „ .....	2

The three points were simultaneously visible on April 5, from 4<sup>h</sup> 32<sup>m</sup> to 4<sup>h</sup> 42<sup>m</sup> P.M.

Brewster's neutral point was perceptibly more distinct than Babinet's at fifteen observations, and less distinct at two observations.

I subjoin a few of my notes, which refer to points of special interest.

March 8, 5<sup>h</sup> 45<sup>m</sup> P.M.—Near the proper position for Arago's neutral point, the positive and negative polarities coalesce upon clouds, with no intervening space or neutral line.

March 9, 6<sup>h</sup> 25<sup>m</sup> A.M.—Hazy, and polarization fluctuating. 10<sup>h</sup> 40<sup>m</sup> A.M.—The polariscope showed a brilliant halo around the sun, which I had not before noticed, but which was afterwards barely visible to the naked eye. 12<sup>h</sup> 10<sup>m</sup> P.M.—Haze continues. Negative polarity remarkably distinct over the face of the sun, and for several degrees north and south.

March 11, 3<sup>h</sup> 50<sup>m</sup> P.M.—Sky covered with thin clouds. A neutral point in the east, 42° above the horizon, and *more than 70° from the antisolar point*, with reversed polarization, or positive below and negative above. 5<sup>h</sup> 25<sup>m</sup>.—A similar point still observable, but about 5° nearer the horizon.

March 12, 6<sup>h</sup> 30<sup>m</sup> A.M.—Cloudy. Polarization positive from east and west horizon nearly to zenith. A similar observation was made March 21 at 6<sup>h</sup> P.M.

March 17, 9<sup>h</sup> 15<sup>m</sup> and 10<sup>h</sup> 40<sup>m</sup> A.M.\*, and March 18, 10<sup>h</sup> 30<sup>m</sup> A.M.†—Very clear. Sun so bright that I was unable to detect the negative polarity between Babinet's neutral point and Brewster's, even by screening the eye from the direct light of the sun.

March 19, 11<sup>h</sup> 5<sup>m</sup> A.M.‡—Halo, visible only through the polariscope. 1<sup>h</sup> P.M.—Snowing.

March 20, 5<sup>h</sup> 25<sup>m</sup> P.M.—Cloudy. Polarization in horizon everywhere positive.

March 24 to 28 inclusive.—On each of these five successive days Brewster's neutral point was remarkably distinct and beautiful.

April 3, 5<sup>h</sup> 40<sup>m</sup> P.M.—Cloudy in west, and polarization positive from zenith to horizon.

Strong reflexion sometimes changes the character of a comparatively weak polarization from positive to negative, or *vice versâ*. A fainter reflexion, by showing whether the bands are interrupted or continuous, often aids in determining the character of the polarization.

The increased refraction of a piece of glass interposed between the polariscope and the sky will frequently show a neutral point which is otherwise invisible.

The normal polarity is often reversed by a stratum of clouds of uniform thickness, especially within the solar primary lemniscate.—*Proceedings of the American Philosophical Society*, vol. x. Feb. 1861.

#### ON OSTROGRADSKY'S HYDROSTATIC PARADOX.

BY CHIEF JUSTICE COCKLE, F.R.S.§

This inference|| seems to me to be erroneous, unless we impress an arbitrary constitution on the fluid, and have recourse to the unne-

\* On steamboat in Raritan Bay.

† At Eagleswood, near Perth Amboy.

‡ In New York.

§ Extract, communicated by the Author, from a Memoir read to the Queensland Philosophical Society on Monday, April 30, 1866.

|| *i. e.* the inference of Ostrogradsky that the shell will be in equilibrium. His paper in the Petersburg Transactions is reprinted in Taylor's 'Scientific Memoirs.'



cessary hypothesis that a fluid is absolutely continuous. Conceive the contraction to be continued until all the matter of the supposed spherical earth is concentrated at its centre, and we formally as well as substantially have the case discussed by Ostrogradsky. About that centre describe geometrically a sphere passing through one of the points of contact of the particles situate on the inner surface of the liquid vault. Then, from the symmetry of the arrangement, we know that the geometrical sphere will pass through all the points of contact of all the particles situated on that surface, and all the points of contact of any one particle will be in one plane. In a plane, through the points of contact, draw geometrical tangents at all the points of contact of any one particle with all the adjacent particles. Then the symmetry of the supposed arrangement shows that the closed figure so formed will be a regular (equilateral and equiangular) polygon. And that symmetry further indicates that each particle will afford the construction of a similar polygon, that all the polygons so formed are equal, and that each side of each polygon is common to two adjacent particles, and forms the edge of a regular polyhedron. But we know that there are only five regular solids or polyhedra,—namely, the regular pyramid (or tetrahedron), bounded by four equal and equilateral triangles; the cube (or hexahedron), by six squares; the octahedron, by eight equal and equilateral triangles; the dodecahedron, by twelve equal and equilateral pentagons; and the icosahedron, by twenty equal and equilateral triangles. Consequently, however we adjust the magnitude of the spherical balls or particles in reference to that of the geometrical sphere, if we require a system of balls such that each ball shall be capable of being placed in contact with the adjacent balls while each shall be equidistant from the centre of the geometrical sphere, we are restricted to systems of four, six, eight, twelve, and twenty balls, each touching the others of the same system as follows: viz. three others in the system of four, four others in the system of six, three others in that of eight, five others in that of twelve, and three others in that of twenty. A case of fluid equilibrium which can only occur where the particles of the fluid do not exceed twenty in number, can scarcely be held to affect the fundamental principle of hydrostatics. And the fact that while the number of regular polygons is unlimited, that of the regular polyhedra is limited, destroys (except in the particular instances just adverted to) the analogy between a line or circle of particles in equilibrium and a sphere of like particles in equilibrium, and prevents it from being urged in support of the new hydrostatical paradox. I do not at present call to mind any investigations in which a perfect continuity of the fluid is assumed, unless probably in some of those of Professor Challis of Cambridge. But even if I am right in thinking that he has assumed it, all the ends that he had in view would probably be equally well served by changing the assumption to that of particles or distances infinitesimally small in comparison with the particles whose motion is discussed, or the mutual distances of the latter particles. At all events an hypothesis assumed for a special purpose ought not to influence the present discussion, unless it explains phenomena to be explained in no other way.—*Queensland Daily Guardian*, Wednesday, May 9, 1866.



CONTRIBUTIONS TOWARDS THE MORE ACCURATE KNOWLEDGE OF  
THE PHENOMENA OF FLUORESCENCE. BY DR. VICTOR PIERRE  
OF PRAG.

The results of this investigation are as follows:—

(1) That the property of exciting fluorescence is not confined to the most refrangible rays of the spectrum, but that rays of any wave-length can in general excite fluorescence.

(2) There is for each substance a definite prismatic colour in which fluorescence first occurs, so that all colours less refrangible than this produce no fluorescence.

(3) It is seldom that this colour is the one which produces the most intense fluorescence; generally it is the next more refrangible rays, but always definite rays for a definite substance.

(4) If rays of a definite colour, that is, of definite wave-length and time of vibration, evoke fluorescence in a substance, not only are rays produced of greater time of vibration than those of the exciting rays, but the rays produced by fluorescence are, for each substance, always the same, whatever be the duration of vibration of the producing ray.

(5) The wave-lengths of the rays produced by fluorescence do not always gradually shade into one another, but there are occasionally jumps, so that rays of a certain length are not developed, in which case the spectrum of the fluorescence-colour is traversed by dark lines; this phenomenon also is independent of the wave-length (direction of vibration) of the exciting rays.

(6) Among the new rays resulting from fluorescence, those are always the most intense whose wave-length is either equal, or very nearly equal, to that of the rays in which fluorescence first occurs; in the latter case, however, it is always larger than that corresponding to the beginning of the fluorescence.

(7) In substances which fluoresce in solution, in case they are soluble in different agents, the solvent occasionally influences the character of the fluorescence, so that, dissolved in different solvents, the same substance fluoresces differently. In one and the same solvent the concentration of the solution only affects the intensity of the fluorescence, but leaves its character unaltered. Above and below that degree of concentration which makes the phenomenon of fluorescence most intense, the intensity of the fluorescence in all parts of the spectrum in which it is at all developed appears to decrease in almost the same ratio; so that with the feeblest development it is distinctly perceptible only in the position of the maximum.

(8) The occurrence of one fluorescing substance with other fluorescing or non-fluorescing substances exercises very different effects on the character of the fluorescence; in many cases it undergoes no change, but in others it is entirely altered. If many fluorescent substances are mixed together, a compound fluorescence is produced, the colour of which, in diffused day- or in direct sunlight, may be very different although the same substances are in both cases mixed together. If the various fluorescent substances do not act on each other so as to alter their fluorescences, such a compound fluorescence may always be resolved into the simple fluorescences of those substances which are contained in the mixture; and so far the

presence of certain substances may be detected by fluorescence in a mixture of different substances, but not in the opposite case.

(9) There are substances which become strongly fluorescent by the addition of acids, and others by the addition of alkalies: in these cases it is immaterial which acid or which alkali is used; the character of the fluorescence is always the same\*. (Hydrochloric and hydriodic acid form an exception, as they destroy fluorescence.)

(10) The light of artificial sources, or such as has passed through coloured media, occasionally produces changes in the fluorescence compared with that of the sunlight, inasmuch as the commencement and maximum fluorescence may fall at other parts of the spectrum.

#### *Connexion between Fluorescence and Phosphorescence.*

It was of some interest to include in my investigations the phenomena of phosphorescence which are so markedly developed by the sulphides of the different earth-metals; and I used for this purpose preparations partly obtained from Albert in Frankfort, and partly from Lenoir in Vienna.

If the prismatic spectrum is projected on one of these phosphorescent bodies, the phenomena are the same as with fluorescent bodies. Phosphorescence begins sometimes in the visible, sometimes in the ultra-violet rays—in short, in different preparations, in different parts of the same spectrum; it has also a maximum (in some substances I found two maxima), and the colour of the light of phosphorescence is the same in the entire extent of the part of the spectrum which excites phosphorescence. If a linear spectrum projected upon such a body be analyzed by a prism, a derived spectrum is also obtained, which in its principal features has the same appearance as that of a fluorescent substance; but the uneven rough surface of this body permits no pure spectrum; a good deal of light is always irregularly scattered, owing to which it was impossible to ascertain with certainty whether there is not here something analogous with compound fluorescence; I imagine that in some of the substances examined something of that kind is the case. The entire appearance which a phosphorescent body offers in the prismatic spectrum is so completely the same as in a fluorescent one, that from this appearance alone it could not at all be decided whether it was a case of fluorescence or of phosphorescence; the difference of the two phenomena consists only in the fact that fluorescence immediately disappears if the incident light is cut off, while phosphorescence continues in this case, though it quickly diminishes in intensity; the phenomena occur just as with a fluorescent liquid in which the concentration is altered to the disappearance of fluorescence. The phenomena is first imperceptible at the side of the commencement and in the ultra-violet, and is finally only perceptible at the positions of maximum. Thus I agree with the statement of Becquerel, that fluorescence and phosphorescence are only distinguished by their duration, inasmuch as the former is at once extinguished with the cessation of the exciting rays, while the latter continues.—*Wiener Berichte*, May 11, 1866.

\* This deportment is, in a certain sense, analogous to that of coloured transparent media, which change their colour by the addition of acids or alkalies. In this also the resulting mixture is independent of the nature of the acid or base added.

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SEPTEMBER 1866.

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XXII. *Reply to Dr. Werner Siemens's Paper "On the Question of the Unit of Electrical Resistance."* By FLEEMING JENKIN, F.R.S.\*

IN the Philosophical Magazine for May, there appeared a translation of a paper "On the Unit of Electrical Resistance" by Dr. Werner Siemens, containing views much at variance with the conclusions of the British-Association Electrical-Standard Committee, and referring frequently to the part I have taken in supporting those conclusions. Dr. Siemens enjoys so high a reputation, that I am anxious to answer his arguments directly, instead of simply referring, as I might do, to the Reports of the Committee, where most of the points have, I think, been already met.

Dr. Siemens has treated of several very distinct questions, which might be divided as follows:—

- (1) What is the best unit of electrical resistance?
- (2) What is the best method of making and reproducing any unit?
- (3) Have Dr. Siemens's proposals and labours met with fair consideration and full acknowledgment by the Committee and by myself?

As to the first point, Dr. Siemens supports as unit the resistance of a prism of mercury 1 metre long and 1 square millimetre section at  $0^{\circ}$  C., or a million times the resistance of a cubic metre of mercury at  $0^{\circ}$ .

The British-Association Committee propose as unit ten million times the absolute electromagnetic unit, or metre per second, as

\* Communicated by the Author.



determined by a Subcommittee consisting of Professor Thomson, Professor Maxwell, Mr. Balfour Stewart, and myself.

The arguments in favour of one or the other of these units should be kept quite distinct from those in favour of the best materials for the reproduction or manufacture of material standards. If mercury be the best material for a permanent standard, any unit can be made of mercury. If mercury be the best material for reproducing a standard, then when the specific resistance of pure mercury in any unit has been determined, mercury can be used for the reproduction of that unit. Conversely, if Dr. Siemens's be the best definition for a unit of resistance upon some independent grounds, then the fact that mercury was a bad substance for constructing or reproducing the unit might not even weaken the arguments in favour of his definition.

Now, apart from the question of manufacture and reproduction, why should a mercury unit be chosen? I see no arguments in Dr. Siemens's paper in favour of his own definition, except perhaps the statement that "mercury is the conductor which is withoutdoubt the best suited to serve as unit of conducting-power."

Dr. Siemens here separates conducting-power from resistance, and seems to think that the specific conducting-powers of materials should be referred to some one standard material, and that the unit of conducting-power may be distinct from the unit of resistance. But conducting-power is naturally defined in calculations as the reciprocal of resistance, the unit of resistance and of conducting-power being the same; there is therefore no need whatever to select any substance as a unit of conducting-power, which would indeed simply introduce confusion into mathematical expressions of electrical relations. The Committee have therefore adopted Professor Thomson's definition of the specific conducting-power of metals as the conducting-power of the wire of unit length and weight (being the reciprocal of the resistance of the same wire). In this way the numbers expressing the specific properties are rendered independent of comparison with any material whatever, whereas, on the other plan, we should always have to ask on whose determination of mercury, silver, or gold &c. the values given were based. Moreover Professor Thomson's plan is infinitely more convenient in calculating from the specific values the actual resistance or conducting-power of any given wire. These considerations absolve me from the necessity of even considering whether, if a unit-material must be selected, mercury would be the best—a question which I nevertheless think might not be decided affirmatively.

Dr. Siemens also claims practical advantages, but does not state their nature. Mercury is little used in telegraphy as compared with copper, German silver, or iron.



A metre long and square millimetre section has a symmetrical sound; but, except in calculating the resistance of prisms of mercury, I know of no practical advantage which it has over any other magnitude. A metre of pure copper weighing a gramme would be more practically useful, for it would serve as an immediate term of comparison with the copper supplied for conducting-wires. A mile of iron wire, of the size generally used in telegraphy, would have a practical advantage in finding the distance of faults. I could give other definitions with practical advantages, but do not know of any practical advantage which has resulted, or could result, from a definition in terms of mercury.

Then even in a mercury unit, no reason is assigned for preferring the particular definition given to any other, such as a metre of mercury, weighing a gramme, or contained in a tube of say 1 millimetre diameter. I do not ask these questions as contending that these definitions are better than Dr. Siemens's, but simply to point out the completely arbitrary nature of his definition.

I have heard in favour of that definition two arguments which, so far as they go, are really in its favour. First, that it was coming into extensive use when the Standard Committee was appointed; secondly, that it was at least an intelligible definition. The first argument is based on truth, though the use of Dr. Siemens's unit was by no means so general as some of his friends suppose. No large English telegraph company used it, nor has it, I believe, been at all adopted in France. Nevertheless I admit that, owing to the undoubtedly excellent manufacture of Messrs. Siemens's resistance-coils, and the convenient arrangements of those coils, his unit was largely used; but this extended use was not, I think, caused by the excellence of his definition. People ordered coils from the most celebrated firm in Europe and took what was given them—the miles of copper wire before 1860, and the mercury units afterwards.

This argument, however, was fully considered by the Committee, but was overthrown by the considerations that changes were yearly being made in the coils supplied, that the definition, being wholly arbitrary and having no intrinsic merit, could not be compared in value with an approximation to the natural unit adopted, and that the use was by no means so general as to outweigh the two previous arguments.

I next come to the question of intelligibility. No doubt most people think they know what a metre of mercury of 1 millimetre section means, and comparatively few understand the definition adopted by the Committee. But who in practical life, or in the use of standards, refers to their definition? What Frenchman, measuring the contents of a brick wall, thinks of the earth's

diameter? what Englishman, using a foot, thinks of pendulums? For practical use the material standard, not the definition, is the important point.

Further than this, the apparently simple definition might lead to gross errors. It requires all Dr. Siemens's skill to produce a mercury unit, if even he can do it. The attempt on the part of any ordinary optician to produce a mercury unit would result in gross discrepancies, which unfortunately might not be discovered until coils had been in use for years. The Committee, therefore, did not think the difficulty of explaining the definition of their unit of any serious importance.

Hitherto I have endeavoured to show that there is no reason to adopt Dr. Siemens's definition more than any other; I have now to show why any other definition should have been preferred to Dr. Siemens's by the Committee.

First to be considered were the practical units—the foot of copper wire, or the mile of iron wire, &c. One objection to these is, that to make them exact is to make them unpractical. Pure metals or specific alloys must have been adopted, and in practice these are never found. Practically no two feet of copper wire or miles of iron wire are alike. There are other arguments on this point which will be found in previous Reports.

I now come to the definition adopted. The reason of this adoption was that the absolute or natural units are those which must necessarily be used in all mathematical calculations of the relations between currents and magnets, according to the existing system of the measurement of magnets. They are, further, most convenient in expressing the relations between all electrical magnitudes themselves. How this is done I have already explained very fully in the Reports which, as Secretary, I had the honour to write for the Committee, and which I am happy to find meet with some approval by Dr. Siemens. Weber, Thomson, and Clerk Maxwell's writings are full of examples: the absolute unit is as natural an expression of electrical resistance as the cubic metre is of capacity when the lineal metre is the unit of length. It is the unit which necessarily expresses resistance, just as the cube necessarily expresses capacity. It would as certainly have been used in all scientific investigations (even if Dr. Siemens's unit had been in universal practical use) as the cubic metre or cubic foot are used in calculation even where the practical measures in use may be the chopin or the gallon. The Committee, therefore, considered that they had no choice in the matter so far as definition was concerned. On the one hand there was a number of arbitrary definitions, on the other the natural unit inevitably used in calculations: could their decision be doubtful?

So far I have argued the matter simply on the ground of definition. Dr. Siemens says that "the resistance-unit must consist of a definition, or be an absolute measure, which can be at any time and in any place reconstructed." I think I am right in understanding these words to mean that Dr. Siemens prefers a mere definition to any material standard whatever, even his own; and I am borne out in this view by his remark, that future and more complete determinations of his unit would become necessary as the exactness of physical measurements progresses; though he anticipates that no practical inconvenience could result from these corrections, as they would be very small. The Committee were of a diametrically opposite opinion: they thought that the one essential quality of a standard was its invariability, that no possible inconvenience would be equal to the continual variation of the standard, making, as it were, the 12 inches of today the 13 inches of tomorrow. No doubt we all believe that the corrections would not be so great or so frequent as this; but what man of science could recommend a periodical tampering with the lengths of the standard metre to bring it more nearly in accordance with some abstract definition? Such changes would on each occasion render almost useless an inconceivable mass of scientific labour. For instance, all Dr. Matthiessen's specific resistances of metals, recorded in Siemens's units, would, since their first issue, have required two or three revisions, and would even now be far from fixed. If, therefore, we can make a permanent unit, I think any permanent unit will be better than any definition; but if a definition alone is to be adhered to, the definition adopted by the Committee is much preferable to that of Dr. Siemens.

Dr. Siemens acknowledges with perfect candour the scientific importance of the determination of Weber's dynamic unit, but thinks that, as the determination of resistances combined with dynamic values rarely occurs, its general use is not of much practical importance. But although the combination of resistances with dynamic values rarely occurs in practice, the combination of resistance with the measurement of quantity, capacity, and currents is of daily occurrence. The unit proposed by Dr. Siemens stood alone and unconnected with any of those measurements. The Committee have adopted a coherent system, in which the current will be equal to the electromotive force divided by the resistance, the quantity to the quantity conveyed by the unit of current in the second, and the capacity to the capacity which, when electrified by the unit electromotive force, will contain the real quantity. Standards for the determination or measurement of all these magnitudes will be issued by the Committee. Dr. Siemens himself very fairly admits that in the British Associa-



tion Reports the argument in favour of this coherent system of measurement is very convincingly put forward. The mercury stands alone an arbitrary definition, while every one of the Committee's units will be an approximation to the natural or mathematical unit. Now this relation between the several units is of practical convenience in the daily testing of submarine cables, and in all other electrical measurements.

But Dr. Siemens says, *first*, your so-called permanent unit does not represent your definition even with reasonable accuracy; and *secondly*, it will not be permanent.

With reference to the first point, Dr. Siemens has fairly pointed out the great difficulties of the determinations; but I think he also admits that the names of those who actually conducted the experiments are some guarantee that care would be taken, and that the names of the Committee at large are a further guarantee that the results would not be adopted without a strong conviction that they were trustworthy. But even if they were not, which I entirely disbelieve, the B.A. unit would not be at all more arbitrary than Dr. Siemens's unit, although I allow there would then be no reason for its adoption except its permanency.

Will it then be permanent? Time alone will show whether any of the ten material standards will remain perfectly permanent; but we have at least as good a guarantee for their permanence as Dr. Siemens has for his.

If his 1864 issue were correct, and I heartily wish we could be sure of this, the B.A. unit would be equal to 1.0486 metre of mercury at 0° C. of 1 square millimetre section; and this resistance can be obtained just as easily as the resistance of one metre. If, therefore, all our material standards vary, we are no worse off than Dr. Siemens. But we have what, while the present discrepancies in mercury-determinations exist, I venture to think is an extremely important addition to our security, in the probability of the permanence of the standards already made. We have all Dr. Siemens has, and a great deal more.

Every additional metal of which the specific resistance is accurately determined gives a fresh guarantee; and it is possible that some day this method of ensuring permanence may be more important than the mere conservation of material standards. As yet I think this is not so.

To sum up the arguments hitherto used.

The mercury unit as defined is arbitrary, varying, has no practical advantage, and forms part of no coherent system of general electrical measurements.

The British-Association unit is based on the natural mathematical unit, is permanent, and has the practical advantage of form-



ing part of a coherent system for other electrical measurements.

Hitherto I have argued wholly on definitions, keeping in reserve all the questions as to how far Dr. Siemens had been successful in producing or reproducing his unit. For instance, when above I say that the mercury unit is varying, I mean that Dr. Siemens intends that it shall vary as better and better determinations are made; and when I say that the B.A. unit is permanent, I mean that the Committee intend it to be permanent. I will now consider how far some of the proposals for the manufacture have been, and are likely to be, practically successful. In arguing this point I am quite willing to abandon all the discrepancies hitherto pointed out in the units supplied by Dr. Siemens. The important question undoubtedly is, not whether Dr. Siemens has from first to last supplied faultless mercury units, but whether any unit can be reproduced by a given length and section or weight of mercury, or any other material. I think I have shown that there is no reason to adopt a metre of mercury of 1 millimetre section as unit of resistance; but mercury may nevertheless be the best substance of which to make units, or by which to reproduce them. I am at a loss to conceive how the two subjects can have been confused as they have been; if platinum be the best metal for a standard weight, we are not therefore obliged to take a cubic metre of platinum as the unit weight.

It is undoubtedly of great importance to have some means of reproducing a unit, in case the original be lost or altered; and Dr. Siemens's experiments are exceedingly valuable, although they can hardly yet be said to be conclusive. Dr. Siemens believes that he can reproduce his unit (and therefore the B.A. unit) at least to within 0.1 per cent. of accuracy, and, when the greatest possible care is used, probably with an almost unlimited exactness. It would, I am sure, give every member of the Committee great pleasure if this fact could be fully established; but it is not yet established. I admit that the discrepancies between the coils exhibited in 1862 have little to do with this point; although I was informed, as I now believe mistakenly, by Dr. Esselbach, that the difference was due to a change in Dr. Siemens's standard. Mr. C. W. Siemens himself at the Royal Society stated that inconvenience had been caused by a premature issue of coils based on an imperfect standard; but after Dr. Siemens's statements, I can feel no doubt that no material alteration has knowingly occurred in this standard. Moreover I admit that errors in early determinations would only show that the reproduction was not very easy, as no one now contends that it is. I further allow that commercial coils cannot be accepted as standards; also that an error in the specific gravity of mercury

in no way affects this part of the question, also that an error in the coefficient of correction for the German-silver copies does not affect the argument; but I do maintain that when Dr. Siemens and Dr. Matthiessen obtain discrepant values after taking all possible care, we must be allowed to suspend our judgment as to which of the two have obtained the value which is most near to truth. According to Dr. Siemens's paper, making a correction in his 1864 standards, as he desires, of 0.287 per cent., the B.A. unit = 1.0486 millimetre of mercury of 1 millimetre section at 0° C. According to Dr. Matthiessen the value is 1.0396. These values are too different to allow us yet to use mercury as a certain means of reproduction.

As soon as one or more independent observers shall obtain really concordant results, they will be accepted by all as a means of checking the permanency of the material standards already made. Till then, I believe the best check will be found in the comparison of the standards themselves, which can be measured with an accuracy approximating at least to within 0.01 per cent., and are correct within this amount, although, owing to a misunderstanding and possible ambiguity of the language employed, Dr. Siemens believed they were not even intended to be so.

I shall not enter into the controversy between Dr. Matthiessen on the one hand, and Mr. Sabine and Dr. Siemens on the other\*. Dr. Matthiessen can take good care of himself, and his reputation is too high to allow us simply to accept Dr. Siemens's results, differing as they do from those of the only other observer who has made researches with similar objects in a distinct laboratory.

Dr. Matthiessen places greater reliance on reproductions by

\* I should, however, be glad to have an explanation upon one point. Dr. Siemens gives a Table showing that the determinations made with two tubes in 1859, and four tubes in 1860 and 1863, differed less than 0.1 per cent., and the most concordant results were obtained in the latest measurements. I venture to point out that, as I understand this statement, it does not prove that the determinations in 1859, 1860, and 1863 were concordant and gave the same unit. It shows that the relative measurements of the several tubes on the three occasions were correctly made within 0.1 per cent., and the relative resistances agreed with these measurements. But this result would have been obtained, however different the mercury might have been on the three occasions, provided of course the three tubes during any comparison were filled from one and the same source. But if by any chance impure mercury was used in 1859 and pure mercury in 1860, the unit as determined by the apparently concordant observations would be very different, and the difference could only be detected by comparison with a material standard assumed as permanent. I should be glad to know whether this comparison was made or not; and if made, with what result. Unless some such comparison has been made, we have no guarantee whatever that the results of the three determinations were really concordant. I do not find any mention of this comparison in Mr. Sabine's or Dr. Siemens's papers; but I may have overlooked it.

lead, or by a gold-silver alloy, than on reproductions by mercury; but until Dr. Siemens, or some other competent observer, also obtains thoroughly concordant results with these materials, I can place no reliance on any of these means of reproduction.

Yet it cannot be denied that the ten so-called permanent standards *may* all vary, and that unless some means of reproduction be discovered before that variation takes place, the unit may be lost. It would therefore be of immense importance to be able to say with certainty that the unit is equal to a certain length and weight of mercury, or lead, or platinum, or any other material; only I protest that if lead, platinum, or mercury be found the best material for this purpose, I will not therefore take the unit length and weight or section of that material as the unit of resistance.

It is this fallacy which I have always endeavoured to expose. No one in the Committee has ever underrated the value of a chemical means of reproduction; on the contrary, money has been freely voted, and committees yearly appointed, having this sole object. Dr. Matthiessen has been opposed to mercury, and to support his views has argued that at any rate hitherto the value of the mercury unit remained unfixed—a perfectly justifiable argument, supported by discrepancies in coils issued, though certainly not conclusive against the possibility of using mercury hereafter. But until this question is settled, the Committee have thought that material standards of very different materials, which remained unaltered in their equality, afforded a fair guarantee of permanency. Should they not remain equal, they can fall back on the length and weight of fresh mercury, lead, or gold-silver alloy which have been or may be found equal to the B.A. unit. Thus, according to Dr. Matthiessen, the ten standards are equal to wires or prisms weighing 1 gramme per metre, and of the following lengths for the various materials:—

Lead . . . . .	0·44307 metre.
Gold-silver alloy . . . . .	0·59952 „
Mercury . . . . .	0·076505 „

We have therefore, as before said, all the guarantees Dr. Matthiessen can have for permanency, with the addition of ten material standards.

Thus, to resume, the reproduction of a standard, whatever that may be, by mercury or any other metal is recognized by the Committee as of great importance, both as an additional guarantee of permanency, and in case of accidental injury; but hitherto they recognize no means of reproduction by mercury or otherwise as established with such authority as to justify its formal adoption, and they see no reason to adopt a unit length



and weight or section of any reproducing material as the unit of electrical resistance.

I now come to the third and personal point, and I enter upon it with great regret. I feel that I must have unconsciously written in a manner calculated to give annoyance, or Dr. Siemens could never have accused me of attacking his propositions "in a way not customary in scientific critiques." I am the more pained by this, as although I have only a slight acquaintance with Dr. Siemens, I may acknowledge with pleasure the friendship of his brother, Mr. C. W. Siemens of London. Certainly, though I have had occasion to differ from Dr. Siemens, and have urged my arguments as forcibly as I could, I never supposed that he or any one would have suspected me of "an intention to throw a false colouring upon the value of his work;" indeed I hardly know in what terms I ought to answer such an imputation.

Meanwhile I prefer to believe that Dr. Siemens will express regret at having in the warmth of controversy made such an accusation. I myself regret that the Report, which as Secretary I had the honour to write and present in 1865, had not been printed before Dr. Siemens wrote his article. The following extract will show the feeling which animated the Committee and myself:—"Thus a difference exists in Dr. Siemens's and Dr. Matthiessen's reproduction of a unit by means of mercury, as pointed out in last year's Report. It is of course probable that differences of this kind will in time disappear, and Dr. Siemens fairly points out that the discrepancy mentioned in last year's Report, between coils made from a very old and those made from a new determination of the mercury unit, affords no criterion of the accuracy with which mercury can now be used as a means of reproduction. Dr. Siemens was the first person who produced numerous sets of coils accurately adjusted; and although unable to recommend the adoption of his unit of resistance, the Committee once more take an opportunity of expressing their sense of the high value of Dr. Siemens's researches on the reproduction of units by means of mercury."

Probably if Dr. Siemens had seen this Report, his article would have been in some respects different. He should remember that if many of our arguments have been directed against his proposition, there are two good reasons for this, inasmuch as his units alone have been able to challenge any comparison with those of the Committee, and he himself has hitherto alone opposed our proposals.

Dr. Siemens refers specially to my Report to the Royal Society on the New Unit of Electrical Resistance. He blames me for using a single determination published in my Report on the



Exhibition of 1862, to force into Tables columns headed "Siemens, Berlin" and "Siemens, London," throws doubt on the accuracy of my observation in 1862, and says that, even if I made no mistake, the coils were adjusted when the art of copying resistances was scarcely known.

First, as to the accuracy of my observation, I may state that the whole of my Report on Dr. Siemens's instruments was submitted in manuscript long before publication to his Firm, in order that any mistakes might be corrected. The discrepancy between the coils was specially pointed out by me verbally, with regret that it should have been found to exist. Messrs. Siemens very kindly sent me a number of valuable corrections, but were unable to explain to my satisfaction the discrepancy between the coils.

I received more than one verbal explanation of that discrepancy. Dr. Esselbach said the standard had been altered; another gentleman said the coils had been touched on their return from the Red Sea; and it was suggested they might have altered with time.

In Mr. Loeffler's written reply on behalf of the firm, a suggestion was made that I might have observed the coils at different temperatures. I pointed out that this would have required  $45^{\circ}$  Fahrenheit as the difference between the coils, and that repeated experiments were made, all with the same result. Messrs. Siemens had the coils returned to them long before the publication of the Report, and did not then deny that a discrepancy existed.

I confess that I believed that they had been made from different standards; nor do I now know the true cause of their difference. In my belief I was strengthened by Mr. Siemens's statement (when the report was read at the Royal Society) that much trouble had been caused by the premature issue of the coils. But I entirely abandon that opinion since I understand that Dr. Siemens states that the mercury standard has never been sensibly changed.

Dr. Siemens throws doubt on the accuracy of my observations by saying that the difference given by me between the sets of coils as 1.2 per cent. was really 1.8 per cent.; but on examination he will see that the difference reported between the two 1862 coils was really 1.2 per cent., though 1.8 per cent. is nearly the difference between one of those coils and the 1864 issue; errors of 0.1 per cent. certainly did not exist in the coils themselves, and therefore the discrepancy could not have resulted from the rudeness of the methods employed to adjust them.

Next, as to the time at which those coils were made, Messrs. Siemens in 1862 stated that both sets exhibited were made at

nearly the same time; they were both extremely well adjusted, as I stated at that time in my Report; and I am not aware that since 1862 any material advance has been made in the adjustments.

I do not quite understand whether Dr. Siemens means to state that the coils called by me "Siemens, London," had been only roughly adjusted by the method of weighing in 1859 and then readjusted in 1862 before exhibition; but whatever be the case, the two sets were equally well adjusted when exhibited, and as good in themselves as any set of coils I have since seen. The charge therefore of unfairness in publishing observations on rude coils, made by an imperfect method, arises from some mistake of Dr. Siemens as to the condition in which the coils were when exhibited by the London firm. Moreover let me point out that in the Report referred to I give the values of coils adjusted by Mr. White of Glasgow in 1859, under Prof. Thomson's supervision, and also exhibited in 1862. These are, and were, in excellent adjustment, with the exception of one coil. They were subjected to the same treatment as to travelling and use as Messrs. Siemens's coils; and I will not do Messrs. Siemens the injustice to suppose that in 1859, when the coils exhibited were first made, they knew less of the art of copying resistances than we did in England.

This value of Prof. Thomson's old unit, based on the old 1859 coils, has been repeated by me in every Table published, although it tells against the absolute unit as a standard, about as much as Messrs. Siemens's old coil tells against the mercury unit. Similarly I have repeated Weber's various discrepant determinations.

To resume. No serious error could have occurred in my experiment without being corrected by Messrs. Siemens at the time, for which they had every opportunity. The coils were not rudely adjusted when exhibited, nor were they even originally made at the time when the art of copying resistances was scarcely known. No explanation of the difference which could be substantiated was given me, and I believed that the difference was probably due to bad reproduction; but I abandon that opinion since I understand Dr. Siemens to say that no change in the standard has been made. I have only repeated their value in Tables in which I repeated still worse discrepancies in so-called absolute determinations, and in which the value of coils as old as those of Dr. Siemens were also given.

Dr. Siemens has himself allowed that the standard in 1864 did not, even by his experiments, truly represent his definition within 0.287 per cent. Surely it was no unfair criticism to point this out; and this is the only point urged by me in the

1864 Report to the Royal Society: and even if it be conceded that the old discrepancies gave no measure of the accuracy of the plan of reproduction, they greatly weaken any argument founded on the priority of Dr. Siemens's unit, and its extended use. One reason for repeating these various values of all units, besides that of showing the discrepancies in those hitherto issued, is that results have been published expressed in each unit.

Dr. Siemens is in error in supposing that Dr. Matthiessen's calculation of the value of the 1862 mercury coils, as compared with the others, rests on the measurement of a copper wire. He had been led into this error, I suppose, by some ambiguity of language; but Dr. Matthiessen's mile of copper wire exhibited in 1862 was a German-silver resistance-coil, as stated in my Juror's Report, and in the Report to the Royal Society. This German-silver coil Dr. Matthiessen still has, and I have the set of German-silver coils called "Thomson's units" in 1862. Both of these have remained constant in their ratio, and the value of all Dr. Siemens's coils has been determined by comparison with them.

A difference of  $1\frac{1}{2}^{\circ}$  C. would therefore by no means account for the discrepancy of 0.5 per cent., which we believe exists between Dr. Siemens's 1862 coils and 1864 standards.

I have now concluded all the remarks I have to make on those parts of Dr. Siemens's paper which are strictly relevant to the matter at issue; but Dr. Siemens, at the end of his paper, makes some criticisms on the historical sketch I gave in the paper above referred to, of the various units of resistance which have been proposed.

I think none of these criticisms would have been made by him if he had observed that I did not profess to give a history of the "progresses in the field of resistance-measurements," as he supposed, but only of the units proposed. A whole book would have to be written to do justice to a history of resistance-measurements, whereas my sketch occupies only three pages.

First, Dr. Siemens complains that I did not mention the sets of resistance-coils made since 1848 in Berlin. I presume these are what I mistakenly called the German mile of No. 8 iron wire. This mistake of mine was not corrected by Messrs. Siemens in 1862, and appears again in the historical sketch. Unfortunately Dr. Siemens's letter to me, giving information for my historical sketch in answer to mine of the 28th February, did not come till the 21st April, while the Report was sent in on the 16th of March, and read on the 6th of April. The value of the coils he refers to is given in the Table annexed to the sketch, and I am sorry that I did not add a note to the reprint giving the exact date of their introduction and their true definition. Dr. Siemens



may, however, observe that I did not think it necessary to give the exact dates at which any of the mile or kilometre units were introduced after those which I was informed were used in 1847 by the Electric and International Company.

Dr. Siemens further criticises my statement that, until about the year 1850, measurements of resistance were chiefly confined to the laboratory; but I confess I think his statement that in 1848 they began to make resistance-coils rather proves than disproves my assertion, especially as I had mentioned that the Electric and International Company had coils in use in 1847.

Next he complains that I do not mention the complete set of resistance-coils made in 1859. But as resistance-coils were then common, I do not see why they should have been mentioned. Does Dr. Siemens mean that he then weighed the coils, instead of using Wheatstone's balance or other electrical adjustment? I had in 1859 one set of coils adjusted by the Wheatstone's balance to within 0.1 per cent., which I use to this day, made by White, under Professor Thomson's directions; and many other sets were in use at the time. These were the coils I used as standards at Birkenhead (not Dr. Siemens's coils, of which I had only very rough specimens of the so-called German mile).

I did not mention this set of practical coils, or any others, my object being to mention new units. I only speak of them now to show that my silence cannot possibly have proceeded from any hostile animus.

Dr. Siemens says my historical sketch is very incomplete; but, beyond the correction in the description of one comparatively unimportant unit, he does not add one definition to those I enumerated, although I quite admit that in all probability some omissions must have occurred. As to Marié Davy's prior proposal for a mercury standard, my own statement is that, though not first in order of time, Dr. Siemens merits especial recognition, owing to the manner in which his proposal was carried out. Is not this what Dr. Siemens claims? The Report was not specially on his unit; and he may observe that Ohm, Wheatstone, Weber, and Thomson, and others of equal rank, have necessarily each but a few lines in the short sketch I wrote.

Next Dr. Siemens complains that I mentioned neither the fact that in 1859 the relative resistances of the conductor and insulator were given in mercury units, nor the method followed to measure the resistance which the insulating covering offered to the electric current and to compare it with that calculated from the specific resistance of the insulated material.

This subject was unconnected with the introduction of any new unit, and was therefore omitted as irrelevant.

If I had mentioned the subject at all, I should first have



mentioned Professor Thomson, who in a lecture in 1857 to the British Association gave the relative specific resistances of the copper and gutta percha of the Atlantic cable. In a note below is an extract from a printed report published in a local paper\*. Next to Professor Thomson I should have mentioned myself, who, acting not under Dr. Siemens's direction, but at the suggestion of Professor Thomson, made in the spring and summer of 1859 experiments on this subject, more complete, I think, than are contained in Dr. Siemens's Red-Sea Report. These results were published at the Meeting of the British Association in 1859, and communicated in a more complete form to the Royal Society; whereas it is not till 1860 that I find any publication by Dr. Siemens on the subject, in a paper read to the British Association in 1860, the very body which had received the two previous communications. He is silent as to both of these. He gives less complete results than those given in the previous year; he gives no experiments on the difference between positive and negative currents, nor any account of the curious effect of electrification due to the time the current has been applied, and without which any record of resistance-measurements is nearly useless. Experiments on both these points are given in my paper. Surely, then, it cannot have been from any hostile feeling to Dr. Siemens that I said nothing about the measurement of the resistance of insulators.

\* Extract from Professor W. Thomson's Lecture before the Members of the British Association at Dublin, 1857, taken from the Glasgow 'North British Daily Mail' of the 4th of September, 1857:—

" . . . . . He had now described the material and the process of manufacture. He would like to say something of the relative qualities of gutta percha and copper as conductors, for they were both conductors—the distinction between non-conductors and conductors being not an absolute distinction, but only a relative distinction. Gutta percha is not a non-conductor, but a very powerful resister of electricity. Gutta percha and every known substance conducted electricity through it. (The lecturer proceeded to explain that, when tested by the galvanometer, there was very little difference in the force of a current sent into 2500 miles of the Atlantic cable, whether the circuit was or was not completed.) This seemed rather hopeless for telegraphing (he continued), where there was so much leakage that the difference could not be discovered between want of insulation and insulation at the remote end. But if there were 49-50ths lost by defective insulation, it would only make the difference between sending a message in nine minutes instead of in eight. The explanation of this was simple, but must be reserved. He then proceeded to allude to the variations of the conducting-power of gutta percha in different temperatures, and gave several comparisons, the result of experiments by Mr. Whitehouse and himself on this subject, and showed that the variations observed in portions of the same material were caused by difference of temperature. At hot temperatures gutta percha resisted twenty million million times as much as copper; at cold temperatures one hundred million million million. . . . ."

Dr. Siemens also speaks of his methods, read to the British Association in 1860, as forming the foundation of the rational system of cable-testing now in use. When writing of what is done in a foreign country, we are often very imperfectly informed as to the literature and progress of that country. I cannot doubt Dr. Siemens never heard of Professor Thomson's lecture or of my papers, or he would in 1860 have mentioned them.

It is equally clear that he has not paid much attention to the mass of evidence given in 1859 before the Board-of-Trade Committee on submarine cables. I have no doubt that he never heard of Professor Thomson's paper published in 1860 in the *Encyclopædia Britannica*, giving all the methods which he claims. If he had seen any of these papers, he never could have thought that he had taught us much by a paper in 1860. The methods described in his interesting paper were quite familiar to Professor Thomson, Latimer Clark, C. F. Varley, myself, and others. The methods are so treated by Professor Thomson in the above article, which deserves to be better known even in England than it is.

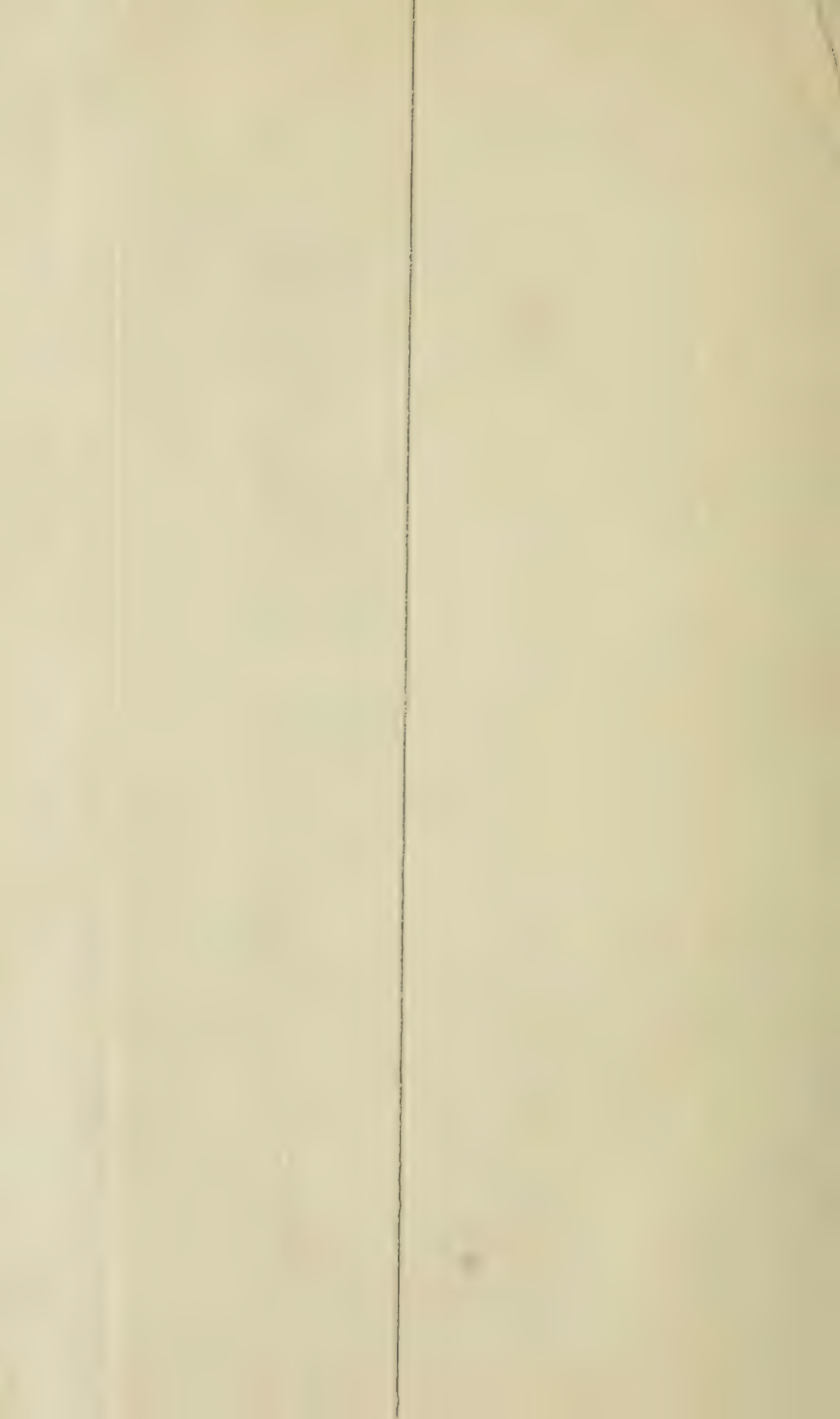
Can Dr. Siemens still think that I avoided mention of all these papers, familiar as they are to me, in order wilfully to be silent as to his work?

Be it well understood that I am making no counter accusation of unfairness. I am sure some of the papers I have referred to were unknown to Dr. Siemens; and probably, with reference to the Report of the Committee of the Board of Trade, as it was only published in 1861, Dr. Siemens may not have observed that the evidence to which I refer was given in 1859.

I can well understand that Dr. Siemens, who has undoubtedly invented these methods independently and has carried them out successfully in important works by a large and able staff, may not have been fully informed as to the progress independently made in England; but to one who is familiar with the papers referred to, his claim to have founded the rational system now in use reads a little strangely. I will not be led into a controversy as to every little improvement in arrangements, or every mathematical formula in use: these improvements are often made independently by many men; and the formulæ are often obvious and necessary deductions from perfectly well known principles: but I do claim for Professor Thomson the honour of having been the first to insist on a measurement of the conducting-power of the copper in submarine cables, and to express the quality of the insulation in terms of resistance, though I said nothing of these things in my Royal-Society Report because they were irrelevant.

I wish in conclusion to say that I believe no English electrician is more fully persuaded of the great services rendered to telegraphy by Dr. Siemens than I am. I know the immense







difference between devising theories in the cabinet, or even trying isolated experiments, and actually carrying out those methods on a large scale by the aid of an organized staff. I concede both merits to Dr. Siemens; and if I have urged my arguments forcibly as to the independence of the English school of electricians of that of Germany, I beg Dr. Siemens to believe that I have done so from no desire to diminish his claims, which indeed I could not do, but only to vindicate myself from what I felt to be a very unmerited suspicion, that of having wilfully omitted to mention his discoveries.

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XXIII. *On the Phenomena observed in the Absorption-spectrum of Didymium.* By R. BUNSEN\*.

[With Two Plates.]

IN a paper which Professor Bahr and I published together, "Upon the Compounds of Erbium and Yttrium"†, we showed that slight differences were observed in the absorption-spectrum of sulphate of didymium, according as the light was allowed to pass through a crystal or through a solution of the salt. Since that time I have found that the erbium- and the didymium-spectrum undergo alteration if polarized light be employed and either the ordinary or the extraordinary ray be allowed to pass through the crystal. I have also found that whilst, when spectroscopes with one prism and with a telescope of moderate power are employed, the spectra of the various didymium compounds do not show any difference, yet most undoubted differences are noticed when more powerful instruments are used.

The alterations which the absorption-spectra exhibit under these circumstances form the subject of the present communication.

In the following experiments two of Steinheil's spectroscopes were used. In the one, which I call the smaller, was placed one flint-glass prism having a refracting angle of  $60^{\circ}$ , and a refracting surface of 30 millims. in diameter, whilst the telescope had a magnifying power of 8: in the other, which I call the larger, were four large prisms of flint glass, one of which had a refracting angle of  $60^{\circ}$ , and the other three each of  $45^{\circ}$ ; the magnifying power of the telescope was 40. The observations with the smaller instrument are reduced to the same scale of measurement as that used in the Table figured in the Philosophical Magazine, S. 4. vol. xxvi. p. 241. With the larger instrument the scale was employed which Kirchhoff adopted in his researches on the solar spectrum.

\* Translated and communicated by Professor Roscoe, from Poggen-dorff's *Annalen*, vol. cxxviii. p. 100.

† *Ann. der Chem. und Pharm.*, vol. cxxvii. p. 1.

The oxide of didymium employed was specially prepared from cerite. The oxalates of the cerite metals were separated from cerium-oxide by heating in the air, dissolving in nitric acid, and boiling with magnesite, and repeating this mode of separation three times with the reprecipitated oxalates.

The separation of the didymium-salt was accomplished in the usual way, by recrystallizing the sulphate twelve times, according to the methods best adapted to effect a complete separation. The crystals exhibited a bluish-red colour; and the oxide prepared from them was of a similar or rather redder tint, but was not the least brown-coloured.

The solution of the salt in water deposited well-formed crystals when allowed slowly to evaporate in a beaker covered with filter-paper during the hot months of summer. They gave on analysis the following numbers:—

Didymium-oxide . . .	46·27
Sulphuric acid . . .	33·73
Water . . . . .	20·00
	<hr/>
	100·00

This corresponds to the formula  $3(\text{DiO}, \text{SO}^3) 8\text{HO}$ , and agrees closely with the following analysis, by Marignac, of the extremely pure salt from which he determined the atomic weight of didymium:—

Didymium-oxide . . .	46·50
Sulphuric acid . . .	33·30
Water . . . . .	20·20
	<hr/>
	100·00

The crystals belong to the monoclinic system. The inclination of the oblique axes was found by measurement to be  $L=61^\circ 45'$ , or close upon the former determinations of Marignac; whilst the relation between the orthodiagonal ( $a$ ), the klinodiagonal ( $b$ ), and the principal axis ( $c$ ) is

$$a : b : c = 0.3283 : 0.6786 : 1.$$

These relations of the axes give the following angles, observed and calculated:—

	Observed.	Calculated.
O P upon $\infty$ P $\infty$ . . .	118 15'	
+ P $\infty$ „ O P . . .	103 7	
O P „ — P . . .	119 40	
$\infty$ P $\infty$ „ + P $\infty$ . . .	138 55	138 38'
O P „ + $\frac{1}{2}$ P . . .	114 0	113 36
+ P „ + $\frac{1}{2}$ P . . .	162 33	162 12
— P „ + P . . .	144 30	144 41
— P „ — P upon O P .	77 30	77 24

The crystal (Plate II. fig. 11) employed in these experiments exhibited a strongly-marked tabular habitus, owing to the growth of the surfaces O P. It was cemented between two thin microscopic glasses with Canada balsam, and was strongly coloured and perfectly clear and transparent.

The plane of polarization of the ordinary and extraordinary rays which pass perpendicular to the surface O P makes with the klinodiagonal and with the orthodiagonal an angle of  $20^\circ$ . Which is the plane of polarization of the ordinary, and which of the extraordinary ray, cannot be settled, as the positions of the optic axes have not been determined. In order to distinguish the spectra of the two rays, a Nicol's prism was placed in front of the crystal, which was so arranged that the light was transmitted in a direction perpendicular to the surface O P; and the crystal so turned round that the plane of polarization of the Nicol coincided with one or other of the two planes. The position of the crystal when the plane of polarization of the Nicol made an angle of nearly  $20^\circ$  with the orthodiagonal I shall call the orthodiagonal position; the other I call the klinodiagonal position.

In the investigation of the spectra of different salts of didymium, a difficulty occurs, in the fact that absorption-spectra, otherwise perfectly similar, assume a different appearance according to the degree of intensity, the breadth of the absorption-bands varying with the thickness and with the proportion of salt contained in the absorbing medium. Such comparative observations, therefore, can only be of value when, in all the comparisons, the light has been acted upon by the same quantities of the absorbent body in passing through the absorbing medium. This condition is fulfilled when the amount of didymium contained in the absorbing medium is inversely proportional to the length of the column through which the light passes. In the comparison of the crystallized and dissolved sulphate with the solutions of other didymium salts this condition was most carefully taken into consideration.

Let the thickness of the layer of crystal through which the light passes be  $l$ , the thickness of the column of solution  $l_1$ ; let the amount of didymium oxide contained in the unit of volume of the crystal be  $d$ , and that in the unit of volume of the solution be  $d_1$ ; then in all the experiments  $d_1$  was so chosen that

$$d_1 l_1 = dl.$$

The crystals used in the experiments had a specific gravity of 2.7153 at  $8^\circ$  C. as a mean of two well-agreeing determinations. 1 cubic centim. of the crystalline mass therefore contains 1.2563 grm. of didymium oxide. The layer of crystal lying between

the faces O P, and through which the light passed, had a thickness of 1.55 millim. as measured by a spherometer. Hence the values of  $d$  and  $l$  are

$$d=1.2563, \quad l=1.55.$$

Solutions of three didymium salts were examined; one of sulphate, one of acetate, and one of chloride. In all three the values of  $d_1$  and  $l_1$  were

$$d_1=0.03414 \text{ grm.}, \quad l_1=57.1 \text{ millim.}$$

The tube (Plate II. fig. 10) used to contain these solutions consists of a thick-walled glass tube of 6 millims. internal diameter, into the ends of which two glass stoppers with plane parallel terminal surfaces were ground. These stoppers were cut out of a piece of plate glass, and fitted by accurate grinding into the tube. In order to prevent the tube from cracking when completely full of liquid, from expansion caused by rise of temperature, a side-tube was melted into the middle of the tube, and this was closed at the end and filled with air. This side-tube also served as a handle to hold the tube horizontal in the cork of the stand, so that the tube could be turned upon the axis of the side-tube and then taken out to be cleaned or refilled. Fig. 1 (Plate II.) gives the position of Fraunhofer's lines, to which the three first spectra are to be reduced. Fig. 2 represents the spectrum obtained by polarized lamplight with the small apparatus when the crystal is placed in the orthodiagonal position; and fig. 3 gives the spectrum by polarized light when the crystal is placed in the klinodiagonal position. Non-polarized light ought to give a spectrum the mean of these two; but it cannot be distinguished from that represented by fig. 3. The differences between figs. 2 and 3 are best seen in the three chief groups of bands near Fraunhofer's lines D, E, and F, as in these groups the bright spaces between the well-defined sharp absorption-bands in fig. 3 become darker in fig. 2, and thus each group of bands attains an indistinct and totally different appearance.

In order to investigate more accurately the changes which occur when polarized light is used, the single groups of bands at D, E, and F were examined by sunlight in the larger instrument. Fig. 5 represents the group of bands near D when the crystal is examined by polarized light in orthodiagonal position; fig. 6 the same group in klinodiagonal position. The spectrum fig. 6 differs from that of fig. 5, inasmuch as the spaces between the single dark bands become brighter, and the band at 1100 disappears, and in its place a new band appears between 1090 and 1095. The group of bands near E undergoes a still more remarkable change. The form of spectrum seen by polarized light in orthodiagonal position (fig. 12, Plate III.) changes to the form represented by fig. 13 when the position of the crystal is



altered to the klinodiagonal one. The five weaker bands disappear almost entirely, whilst only a slight alteration is noticed in the shade of the bands between 1557 and 1570; but at 1476 a new band appears. The alterations produced in the group of bands near the line F are the least visible. Fig. 17 represents this group: it exhibits such slight alterations in the relative brightness of the absorption-bands viewed with polarized light, either in the orthodiagonal or klinodiagonal position of the crystal, that these differences cannot be distinctly made out, especially when viewed by the somewhat weak light which the solar spectrum possesses near F. The same observation was made with several other bands; and their description, for a similar reason, is not given.

All these differences in the absorption-spectra occurring with polarized light resemble the absorption-phenomena which tourmaline exhibits under similar circumstances. The property which crystallized didymium-sulphate possesses, of absorbing differently the ordinary and extraordinary rays, is in its nature identical with that which makes tourmaline so valuable in optical experiments.

The solution of the crystals in water gives another spectrum, differing, again, from both the foregoing. This is represented on Plate II. fig. 4. Here also the three chief groups of bands are situated near D, E, and F, but they are still more confused than in the spectrum obtained when the crystal is placed in the orthodiagonal position (fig. 2).

Some of the maxima of absorption do indeed show a small but perceptible change of form: thus, for instance, the band 27 to 31 of the crystal-spectrum disappears, whilst a new but faint band becomes visible at 30 in the spectrum of the solution.

Very remarkable and noteworthy are the small alterations in position which occur in the minima of brightness in the didymium-spectrum, dependent upon the nature of the compound in which the metal occurs. These changes are too minute to be seen with the small, though seen with the larger instrument; I have as yet only investigated them completely in the case of three didymium-salts, viz. the chloride, sulphate, and acetate. It is, however, more than probable that these same phenomena will also be found to occur with other solutions, and with the absorption-spectra of other crystals of didymium-salts, and perhaps may be exhibited with the luminous spectra of the oxide and other compounds of didymium. The difficulty of obtaining a variety of well-crystallized didymium-salts of sufficient transparency has prevented me from pursuing the subject further in this direction. Plate II. figs. 7, 8, and 9 represent the group of bands near D of didymium chloride, sulphate, and acetate, in the

order in which these salts are mentioned. Plate III. figs. 14, 15, and 16 represent the group of bands near E for these salts in the same order, and figs. 18, 19, and 20 the same for the group near F.

The atomic weight of didymium-chloride is 95·9, and that of the anhydrous acetate 106·9. It will be noticed that all the groups of bands in the case of the salts under examination approach the red end of the spectrum in the order of their increasing atomic weights.

These differences here noticed in the absorption-spectra of different didymium-compounds cannot, in our present complete state of ignorance of any general theory for the absorption of light in absorptive media, be connected with other phenomena. They remind one of the slight and gradual alterations in pitch which the notes from a vibrating elastic rod undergo when the rod is weighted, or of the change of tone which an organ-pipe exhibits when the tube is lengthened.

#### XXIV. On the Origin of Muscular Power.

By E. FRANKLAND, F.R.S.\*

UNDER this title there appeared in a recent Number of the Philosophical Magazine an able article by Professors Fick and Wislicenus†, in which these gentlemen describe the results of experiments made upon themselves before, during, and after an ascent of the Faulhorn in Switzerland. In these experiments the amount of measured work performed in the ascent of the mountain was shown to exceed, by more than three-fourths, the amount which it would be theoretically possible to realize from the maximum amount of muscle-oxidation indicated by the total quantity of nitrogen in the urine.

The data afforded by these experiments appear to me to render utterly untenable the theory that muscular power is derived from muscle-oxidation. Nevertheless, in the application of these data to the problem under consideration, one important link was found to be wanting, viz. the amount of actual energy generated by the oxidation of a given weight of muscle in the human body. Fick and Wislicenus refer to this missing link in the following words:—"The question now arises, what quantity of heat is generated when muscle is burnt to the products in which its constituent elements leave the human body through the lungs and kidneys? At present, unfortunately, there are not the experimental data required to give an accurate answer to this important question; for neither the heat of combustion of muscle, nor of the nitrogenous *residue* of muscle (urea), is known."

\* Communicated by the Author.

† Phil. Mag. vol. xxxi. p. 485.

Owing to the want of these data, the numerical results of the experiment of Fick and Wislicenus are rendered less conclusive against the hypothesis of muscle-oxidation than they otherwise would have been; whilst similar determinations which have been made by Edward Smith, Haughton, Playfair, and others are even liable to a total misinterpretation from the same cause.

I have endeavoured to supply this want by the calorimetrical determination of the actual energy evolved by the combustion of muscle and of urea in oxygen: but, inasmuch as uric and hippuric acids frequently appear in the urine as products of a less perfect muscle-oxidation, I have also determined the calorific value of these substances, and have added purified albumen and beef fat to the list. Creatin would also have been included; but, although I was furnished with an ample supply of this substance through the kindness of Dr. Dittmar, all attempts to burn it in the calorimeter were fruitless. In numerous trials under varied conditions it always exploded violently on ignition.

The determination of the actual energy developed by the combustion of the above-named substances is surrounded by formidable difficulties, which have probably prevented their previous execution. It is impossible to effect their complete combustion in oxygen gas, under conditions which permit of the accurate measurement of the heat evolved; but preliminary experiments showed that complete oxidation could be secured by deflagration with potassic chlorate; and, although this method is doubtless inferior in accuracy to the calorimetrical methods usually employed, it is hoped that, with the corrections described below, the results obtained merit sufficient confidence to render them useful in subsequent discussions of this and allied subjects. The determinations were made in a calorimeter devised some years ago by Lewis Thompson, and which I have repeatedly used with satisfaction in other determinations of a like kind. This instrument consists of a copper tube made to contain a mixture of potassic chlorate with the combustible substance, and which can be enclosed in a kind of diving-bell, also of copper, and so lowered to the bottom of a suitable vessel containing a known quantity (2 litres) of water. The experiments were conducted in the following manner:—19·5 grams\* of chlorate of potash, to which about one-eighth of manganic oxide was added, were intimately mixed with a known weight (generally about 2 grams) of the substance whose thermal value was to be determined; and the mixture being then placed in the copper tube above mentioned, a small piece of cotton thread, previously

\* I follow the example of the Registrar-General in abbreviating the French word *gramme* to gram.



steeped in potassic chlorate and dried, was inserted in the mixture. The temperature of the water in the calorimeter was now carefully ascertained by a delicate thermometer, and, the end of the cotton thread being ignited, the tube with its contents was placed in the copper bell and lowered to the bottom of the water. As soon as the combustion reached the mixture, a stream of gases issued from numerous small openings at the lower edge of the bell and rose to the surface of the water—a height of about 10 inches. At the termination of the deflagration, the water was allowed free access to the interior of the bell, by opening a stopcock connected with the bell by a small tube rising above the surface of the water in the calorimeter. The gases in the interior of the bell were thus displaced by the incumbent column of water; and by moving the bell up and down repeatedly, a perfect equilibrium of temperature throughout the entire mass of water was quickly established. The temperature of the water was again carefully observed; and the difference between this and the previous observation gives the calorific power, or the potential energy, of the substance consumed, expressed as heat.

The value thus obtained, however, is obviously subject to the following corrections:—

1. The amount of heat absorbed by the calorimeter and apparatus employed: *to be added.*

2. The amount of heat carried away by the escaping gases after issuing from the water: *to be added.*

3. The amount of heat due to the decomposition of the chlorate of potash employed: *to be deducted.*

4. The amount of heat equivalent to the work performed, by the gases generated, in overcoming the pressure of the atmosphere: *to be added.*

Although the errors due to these causes to some extent neutralize each other, there is still an outstanding balance of sufficient importance to require that the necessary corrections should be carefully attended to.

The amount of error from the first cause was once for all experimentally determined, and was added to the increase of temperature observed in each experiment.

The amount of heat carried away by the escaping gases after issuing from the water may be divided into two items, viz.:—

$\alpha$ . The amount of heat rendered latent by the water which is carried off by the gases in the form of vapour.

$\beta$ . The amount of heat carried off by these gases by reason of their temperature being above that of the water from which they issue.

It was ascertained that a stream of dry air passed through the water of the calorimeter at about the same rate and for the



same period of time as the gaseous products of combustion, depressed the temperature of the water by only  $0^{\circ}\cdot02$  C.

By placing a delicate thermometer in the escaping gases, and another in the water, no appreciable difference of temperature could be observed. Both these corrections may therefore be safely neglected.

The two remaining corrections can be best considered together, since a single careful determination eliminates both. When a combustible substance is burnt in gaseous oxygen, the conditions are essentially different from those which obtain when the same substance is consumed at the expense of the combined or solid oxygen of potassic chlorate. In the first case the products of combustion, when cooled to the temperature of the water in the calorimeter, occupy less space than the substances concerned in the combustion, and therefore no part of the energy developed is expended in external work—that is, in overcoming the pressure of the atmosphere. In the second case both the combustible and the supporter of combustion are in the solid condition, whilst a considerable proportion of the products of combustion are gases. The generation of the latter cannot take place without the performance of external work; for every cubic inch produced must obviously, in overcoming atmospheric pressure, perform an amount of work equivalent in round numbers to the lifting of a weight of 15 lbs. to the height of one inch. In performing this work the gases are cooled, and consequently less heat is communicated to the water of the calorimeter. Nevertheless the loss of heat due to this cause is but small. Under the actual conditions of the experiments detailed below, its amount would only have increased the temperature of the water in the calorimeter by  $0^{\circ}\cdot07$  C. Even this slight error is entirely eliminated by the final correction which we have now to consider.

It is well known that the decomposition of potassic chlorate into potassic chloride and free oxygen is attended with the evolution of heat: if a few grains of manganic oxide, or, better, of ferric oxide, be dropped into an ounce or two of fused potassic chlorate, which is slowly disengaging oxygen, the evolution of gas immediately proceeds with great violence, and the mixture becomes visibly red-hot, although the external application of heat be discontinued from the moment when the metallic oxide is added. The latter remains unaltered at the close of the operation. It is thus obvious that potassic chlorate, on being decomposed, furnishes considerably more heat than that which is necessary to gasify the oxygen which it evolves. It was therefore necessary to determine the amount of heat thus evolved by the quantity of potassic chlorate (9·75 grms.) mixed

with one gram of the substance burnt in each of the following determinations. This was effected by the use of two copper tubes, the one placed within the other. The interior tube was charged with a known weight of the same mixture of potassic chlorate and manganic oxide as that used for the subsequent experiments, whilst the annular space between the two tubes was filled with a combustible mixture of chlorate and spermaceti, the calorific value of which had been previously ascertained. The latter mixture was ignited in the calorimeter as before; and the heat generated during its combustion effected the complete decomposition of the chlorate in the interior cylinder, as was proved by a subsequent examination of the liquid in the calorimeter, which contained no traces of undecomposed chlorate. The following are the results of five experiments thus made, expressed in units of heat, the unit being equal to 1 gram of water raised through  $1^{\circ}$  C. of temperature.

First experiment . . . .	340
Second experiment . . . .	300
Third experiment . . . .	375
Fourth experiment . . . .	438
Fifth experiment . . . .	438
	<hr/>
	1891
Mean . . . . .	378

This result was confirmed by the following experiments:—

(1) Starch was burnt, first, in a current of oxygen gas, and secondly by admixture with potassic chlorate and manganic oxide.

Heat-units furnished by 1 grm. of starch burnt	}	4290
with 9.75 grms. of potassic chlorate . . . .		
Heat-units furnished by the same weight of starch	}	3964
burnt in a stream of oxygen gas . . . .		
Difference . . . . .		<hr/> 326

(2) Phenylie alcohol was burnt with potassic chlorate, and the result compared with the calorific value of this substance as determined by Favre and Silbermann.

Heat-units furnished by 1 grm. of phenylie alcohol burnt with 9.75 grms. potassic chlorate.	}	8183
Heat-units furnished by 1 grm. of phenylie alcohol when burnt with gaseous oxygen (Favre and Silbermann) . . . . .		
	}	7842
Difference . . . . .		<hr/> 341

These three determinations of the heat evolved by the decomposition of 9.75 grms. of potassic chlorate, furnishing the num-

bers 378, 326, and 341, agree as closely as could be expected when it is considered that all experimental errors are necessarily thrown upon the calorific value of the potassic chlorate.

The mean of the above five experimental numbers was in all cases deducted from the actual numbers read off in the following determinations.

It was ascertained by numerous trials that all the potassic chlorate was decomposed in the deflagrations, and that but mere traces of carbonic oxide were produced.

Joule's mechanical equivalent of heat was employed, viz. 1 kilog. of water raised  $1^{\circ}$  C. = 423 metrekilogs.

The following results were obtained :—

Actual Energy developed by 1 grm. of each substance when burnt in Oxygen.

Name of substance (dried at $100^{\circ}$ C.).	Heat-units.					Metre- kilogs. of force. (Mean.)
	1st Exp.	2nd Exp.	3rd Exp.	4th Exp.	Mean.	
Beef muscle purified by repeated wash- ing with ether ...	5174	5062	5195	5088	5103	2161
Purified albumen...	5009	4987	.....	.....	4998	2117
Beef fat .....	9069	.....	.....	.....	9069	3841
Hippuric acid .....	5330	5437	.....	.....	5383	2280
Uric acid .....	2645	2585	.....	.....	2615	1108
Urea.....	2121	2302	2207	2197	2206	934

It is evident that the above determination of the actual energy developed by the combustion of muscle in oxygen represents more than the amount of actual energy produced by its oxidation within the body, because when muscle burns in oxygen its carbon is converted into carbonic acid, and its hydrogen into water, the nitrogen being to a great extent evolved in the elementary state; whereas when muscle is most completely consumed in the body the products are carbonic acid, water, and urea: the whole of the nitrogen passes out of the body as urea, a substance which still retains a considerable amount of potential energy. Dry muscle and pure albumen yield, under these circumstances, almost exactly one-third of their weight of urea; and this fact, together with the above determination of the actual energy developed on the combustion of urea, enables us to deduce with certainty the amount of actual energy developed by muscle and albumen respectively when consumed in the human body. It is as follows :—

Actual Energy developed by 1 grm. of each substance when consumed in the body.

Name of substance (dried at 100° C.).	Heat-units. (Mean.)	Metrekilogs. of force. (Mean.)
Beef muscle purified by ether ...	4368	1848
Purified albumen .....	4263	1803

Interpolating the data thus obtained into the results of Fick and Wislicenus's experiments, let us now compare the amount of measured and calculated work performed by each of the experimenters during the ascent of the Faulhorn, with the actual energy capable of being developed by the maximum amount of muscle that could have been consumed in their bodies, this amount being represented by the total quantity of nitrogen excreted in each case during the ascent and for six hours afterwards.

	Fick.	Wislicenus.
Weight of dry muscle consumed .....	37·17 grms.	37·00 grms.
Actual energy capable of being produced by the consumption of 37·17 and 37·00 grms. of dry muscle in the body .....	68,690 metrekilogs.	68,376 metrekilogs.
Measured work performed in the ascent (external work) .....	129,096 metrekilogs.	148,656 metrekilogs.
Calculated circulatory and respiratory work performed during the ascent (internal work) .....	30,541 metrekilogs.	35,631 metrekilogs.
Total ascertainable work performed .	{ 159,637 metrekilogs.	184,287 metrekilogs.

The actual energy capable of being produced by the consumption of 37·17 and 37·00 grms. of dry muscle in the body was *estimated* by Fick and Wislicenus at 106,250 and 105,825 metrekilogs.

The experimental determination of the actual energy developed by muscle-oxidation renders it now abundantly evident that the muscular power expended by these gentlemen in the ascent of the Faulhorn could not be exclusively derived from the oxidation either of their muscles or of other nitrogenous constituents of their bodies, since the maximum of power capable of being derived from this source, even under very favourable assumptions, is in both cases less than one-half of the work actually



performed; but the deficiency becomes much greater if, as Fick and Wislicenus have done, we take into consideration the fact that the actual energy developed by oxidation or combustion cannot be wholly transformed into mechanical work. In the best-constructed steam-engine, for instance, only one-tenth of the actual energy developed by the burning fuel can be obtained in the form of mechanical power; and in the case of man, Helmholtz estimates that not more than one-fifth of the actual energy developed in the body can be made to appear as external work. The experiments of Heidenhain, however, show that under favourable circumstances a muscle may be made to yield, in the shape of mechanical work, as much as one-half of the actual energy developed within it, the remainder assuming the form of heat. Taking, then, this highest estimate of the proportion of mechanical work capable of being got out of actual energy, it becomes necessary to multiply by 2 the above numbers representing the ascertainable work performed, in order to express the actual energy involved in the production of that work. We then get the following comparison of the actual energy capable of being developed by the amount of muscle consumed, with the actual energy necessary for the performance of the work executed in the ascent of the Faulhorn.

	Fick.	Wislicenus.
	metrekilogs.	metrekilogs.
Actual energy capable of being produced by muscle-metamorphosis. }	68,690	68,376
Actual energy expended in work performed .....	319,274	368,574

Thus, taking the average of the two experiments, it is evident that scarcely one-fifth of the actual energy required for the work performed could be obtained from the amount of muscle consumed.

Interpreted in the same way, previous experiments of a like kind prove the same thing, though not quite so conclusively. To illustrate this, I will here give a summary of three sets of experiments,—the first, made by Dr. E. Smith upon prisoners engaged in treadmill labour; the second, by the Rev. Dr. Haughton upon military prisoners engaged in shot drill; and the third, adduced by Playfair, and made upon pedestrians, pile-drivers, men turning a winch, and other labourers.

### *Treadwheel Experiments.*

A treadwheel is a revolving drum with steps placed at distances of 8 inches, and the prisoners are required to turn the wheel downwards by stepping upwards. Four prisoners, designated

below as A, B, C, and D, were employed in these experiments; and each worked upon the wheel in alternate quarters of an hour, resting in a sitting posture during the intervening quarters. The period of actual daily labour was  $3\frac{1}{2}$  hours. The total ascent per hour 2160 feet, or per day 1·432 mile. The following are the results:—

## Treadweel Work. (E. Smith.)

	Weight in kilogs.	Ascent in metres.	Days occupied in ascent.	External work performed in metre-kilogs.	Total nitrogen evolved.	Weight of dry muscle corresponding to nitrogen.
A	47·6	23,045	10	1,096,942	grms. 171·3	grms. 1101·2
B	49	23,045	10	1,129,205	174·5	1121·7
C	55	20,741	9	1,140,755	168·0	1080·1
D	56	20,741	9	1,161,496	159·3	1024·3

In these experiments the measured work was performed in the short space of  $3\frac{1}{2}$  hours, whilst the nitrogen estimated was that voided in the shape of urea in twenty-four hours. It will therefore be necessary to add to the measured work that calculated for respiration and circulation for the whole period of twenty-four hours. This amount of internal work was computed from the estimates of Helmholtz and Fick as follows:—

## Internal Work. (Helmholtz and Fick.)

	Work performed.	Actual energy required.
Circulation of the blood during 24 hours at 75 pulsations per minute } Respiration for 24 hours at 12 pulsations per minute } Statical activity of muscles ..... Peristaltic motion .....	metrekilogs.* 69,120 10,886 Not determined. " "	metrekilogs. 138,240 21,772 Not determined. " "
	80,006	160,012

Taking this estimate for internal work, the average results of the treadwheel experiments may be thus expressed:—

\* Since making use of this number I find that Donders estimates the work of the heart alone for twenty-four hours at 86,000 metrekilograms, a figure which is higher than that used above for the combined work of circulation and respiration.

*Treadwheel Work.*

Average external work per man per day . . . . .	}	119,605 metrekilogs.
Average nitrogen evolved per man per day . . . . .		
Weight of dry muscle corresponding to average nitrogen evolved per day	}	114 "
Actual energy producible by the consumption of 114 grms. dry muscle in the body . . . . .		
	}	210,672 metrekilogs.
Average actual energy developed in the body of each man, viz.		
External work . . . . .	$119,605 \times 2 =$	239,210 metrekilogs.
Circulation . . . . .	$69,120 \times 2 =$	138,240 "
Respiration . . . . .	$10,886 \times 2 =$	21,772 "
		399,222 "

In these experiments the conditions were obviously very unfavourable for the comparison of the amount of actual energy producible from muscle-metamorphosis with the quantity of actual energy expended in the performance of estimable work, since, during that portion of the twenty-four hours not occupied in the actual experiment, a large amount of unestimable internal work, such as the statical activity of the muscles, peristaltic motion, &c., was being performed. Nevertheless these experiments show that the average actual energy developed in producing work in the body of each man was nearly twice as great as that which could possibly be produced by the whole of the nitrogenous matter oxidized in the body during twenty-four hours. It must also be remarked that the prisoners were fed upon a nitrogenous diet containing 6 ounces of cooked meat without bone—a diet which, as is well known, would favour the production of urea.

*Shot-drill Experiments.*

The men employed for these experiments were fed exclusively upon a vegetable diet, and they consequently secreted a considerably smaller amount of nitrogen than the flesh-eaters engaged in the treadwheel work; the other conditions were, however, equally unfavourable for showing the excess of work performed over the amount derivable from muscle-metamorphosis.

In shot drill each man lifts a 32-lb. shot from a tressel to his breast, a height of 3 feet; he then carries it a distance of 9 feet and lays it down on a similar support, returning unloaded. Six of these double journeys occupy one minute. The men were daily engaged with

Shot drill . . . . .	3 hours.
Ordinary drill . . . . .	11 1/4 "
Oakum-picking . . . . .	3 1/2 "

The total average daily external work was estimated by Haughton at 96,316 metrekilogs. per man. The following is a condensed summary of the results of these experiments :—

*Military Vegetarian Prisoners at Shot Drill. (Haughton.)*

Average external work per man per day . . . . .	}	96·316 metrekilogs.
Average nitrogen evolved per man per day . . . . .		
Weight of dry muscle corresponding to average nitrogen evolved per day	}	77·9 „
Actual energy producible by the consumption of 77·9 grms. of dry muscle in the body . . . . .		
Average actual energy developed daily in the body of each man, viz.		

External work  $96,316 \times 2$  . . . = 192,632 metrekilogs.

Internal work . . . . . = 160,012 „

352,644 „

Owing chiefly to the vegetable diet of these prisoners, this result is more conclusive than that obtained upon the treadwheel, the amount of work actually performed being considerably more than twice as great as that which could possibly be obtained through the muscle-metamorphosis occurring in the bodies of the prisoners.

*Playfair's Determinations.*

In these determinations the number 109,496 metrekilograms was obtained as the average amount of daily work performed by pedestrians, pile-drivers, porters, paviours, &c.; but as the amount of muscle-consumption is calculated from the nitrogen taken in the food, the conditions are as unfavourable as possible with regard to the point I am seeking to establish; for it is here assumed, not only that all the nitrogen taken in the food enters the blood, but also that it is converted into muscle, and is afterwards oxidized to carbonic acid, water, and urea.

The following are the results, expressed as in the previous cases :—

*Hard-worked Labourer (Playfair).*

	Work performed.	Actual energy required.
	metrekilogs.	metrekilogs.
Daily labour (external work)....	109,496	218,992
Internal work .....	80,006	160,012
	189,502	379,004

Actual energy capable of being produced from 5·5 oz. (155·92 grms.) of flesh-formers contained in the daily food of the labourer ..... 288,140



Thus, even under the extremely unfavourable conditions of these determinations, the actual work performed exceeded that which could possibly be produced through the oxidation of the nitrogenous constituents of the daily food by more than 30 per cent.

We have seen, therefore, in the above four sets of experiments, interpreted by the data afforded by the combustion of muscle and urea in oxygen, that the transformation of tissue alone cannot account for more than a small fraction of the muscular power developed by animals; in fact this transformation goes on at a rate almost entirely independent of the amount of muscular power developed. If the mechanical work of an animal be doubled or trebled, there is no corresponding increase of nitrogen in the secretions; whilst it was proved, on the other hand, by Lawes and Gilbert as early as the year 1854, that animals under the same conditions as regarded exercise, had the amount of nitrogen in their secretions increased twofold by merely doubling the amount of nitrogen in their food. Whence, then, comes the muscular power of animals? What are the substances which, by their oxidation in the body, furnish the actual energy whereof a part is converted into muscular work? In the light of the experimental results detailed above, can it be doubted that a large proportion of the muscular power developed in the bodies of animals has its origin in the oxidation of non-nitrogenous substances? For, whilst the secretion of nitrogen remains nearly stationary under widely different degrees of muscular exertion, the production of carbonic acid increases most markedly with every augmentation of muscular work, as is shown by the following tabulated results of E. Smith's highly important experiments upon himself, regarding the amount of carbonic acid evolved under different circumstances\*.

Excretion of carbonic acid during rest and muscular exertion:—

	Carbonic acid per hour.
During sleep . . . . .	19·0 grams.
Lying down, and sleep approaching .	23·0 „
In a sitting posture . . . . .	29·0 „
Walking at the rate of 2 miles per hour	70·5 „
Walking at the rate of 3 miles per hour	100·6 „
On the treadwheel, ascending at the rate of 28·65 feet per minute . . .	189·6 „

It is admitted on all hands that food, and food alone, is the ultimate source from which muscular power is derived; but the above determinations and considerations prove conclusively, first, that the non-nitrogenous constituents of the food, such as

\* Phil. Trans. for 1859, page 709.

starch, fat, &c., are the chief sources of the actual energy which becomes partially transformed into muscular work ; and secondly, that the food does not require to become organized tissue before its metamorphosis can be rendered available for muscular power, its digestion and assimilation into the circulating fluid (the blood) being all that is necessary for this purpose. It is, however, by no means the non-nitrogenous portions of food alone that are capable of being so employed—the nitrogenous also, inasmuch as they are combustible, and consequently capable of furnishing actual energy, might be expected to be available for the same purpose ; and such an expectation is confirmed by the experiments of Savory upon rats\*, which show that these animals can live for weeks in good health upon food consisting almost exclusively of muscular fibre. Even supposing these rats to have performed no external work, nearly the whole of their internal muscular work must have had its source in the actual energy developed by the oxidation of their strictly nitrogenous food.

It can scarcely be doubted, however, that the chief use of the nitrogenous constituents of food is for the renewal of muscular tissue—the latter, like every other part of the body, requiring a continuous change of substance ; whilst the chief function of the non-nitrogenous is to furnish, by their oxidation, the actual energy which is in part transmuted into muscular force.

The combustible food and oxygen coexist in the blood which courses through the muscle ; but when the muscle is at rest, there is no chemical action between them. A command is sent from the brain to the muscle, the nervous agent determines oxidation. The potential energy becomes actual energy, one portion assuming the form of motion, another appearing as heat. *Here is the source of animal heat, here the origin of muscular power!* Like the piston and cylinder of a steam-engine, the muscle itself is only a machine for the transformation of heat into motion ; both are subject to wear and tear, and require renewal ; but neither contributes in any important degree, by its own oxidation, to the actual production of the mechanical power which it exerts.

From this point of view it is interesting to examine the various articles of food in common use, as to their capabilities for the production of muscular power. I have therefore made careful estimations of the calorific value of different materials used as food, with the same apparatus and in the same manner as described above for the determination of the actual energy in muscle, urea, &c. The results are embodied in the following series of Tables ;

\* The Lancet, 1863, pages 381 and 412.

but it must be borne in mind that it is only on the condition of the food being digested and passed into the blood, that the results given in these Tables are realized. If, for instance, sawdust or paraffin oil had been experimented upon, numbers would have been obtained for these substances, the one about equal to that assigned to starch, and the other surpassing that of any article in the Tables; but these numbers would obviously have been utterly fallacious, inasmuch as neither sawdust nor paraffin oil is, to any appreciable extent, digested in the alimentary canal. Whilst the force-values experimentally obtained for the different articles in these Tables must therefore be understood as the maxima assignable to the substances to which they belong, yet it must not be forgotten that a large majority of these substances appear to be completely digestible under normal circumstances.

TABLE I.—Results of Experiments with Food dried at 100° C., in heat-units.

Name of food.	Heat-units. 1st Exp.	Heat-units. 2nd Exp.	Heat-units. 3rd Exp.	Heat-units. (Mean.)
Cheshire cheese .....	6080	6149	.....	6114
Potatoes .....	3752	.....	.....	3752
Apples .....	3776	3562	.....	3669
Mackerel .....	5994	6134	.....	6064
Oatmeal (not dried) .....	4143	4018	3857	4004
Lean beef .....	5271	5260	5410	5313
White of egg .....	4823	4940	4927	4896
Carrots .....	3776	3759	.....	3767
Pea-meal (not dried) .....	3866	4006	.....	3936
Flour (not dried) .....	3941	3931	.....	3936
Arrowroot (not dried) .....	3923	3902	.....	3912
Butter .....	7237	7291	.....	7264
Ham boiled and lean .....	4188	4498	.....	4343
Lean veal .....	4459	4595	4488	4514
Hard-boiled egg .....	6455	6187	.....	6321
Yolk of egg .....	6460	.....	.....	6460
Isinglass .....	4520	4520	.....	4520
Cabbage .....	3809	3744	.....	3776
Whiting .....	4520	4520	.....	4520
Ground rice (not dried) .....	3802	3824	.....	3813
Cod-liver oil .....	9134	9080	.....	9107
Cocoa nibs (not dried) .....	6809	6937	.....	6873
Residue of milk .....	5066	5120	.....	5093
Bread crumb .....	3984	3984	.....	3984
Bread crust (not dried) .....	4459	.....	.....	4459
Lump sugar (not dried) .....	3403	3294	.....	3348
Commercial grape-sugar (not dried) ..	3277	3277	.....	3277
Residue from bottled ale .....	3776	3744	.....	3760
Residue from bottled stout .....	6348	6455	.....	6401

TABLE II.—Actual Energy developed by 1 gram of various articles of Food when burnt in Oxygen.

Name of food.	Heat-units.		Metrekilograms of force.		Per cent. of water.
	Dry.	Natural condition.	Dry.	Natural condition.	
Cheese (Cheshire) .....	6114	4647	2589	1969	24.0
Potatoes .....	3752	1013	1589	429	73.0
Apples .....	3669	660	1554	280	82.0
Oatmeal .....	.....	4004	.....	1696	
Flour .....	.....	3936	.....	1669	
Pea-meal .....	.....	3936	.....	1667	
Ground rice .....	.....	3813	.....	1615	
Arrowroot .....	.....	3912	.....	1657	
Bread crumb .....	3984	2231	1687	945	44.0
Bread crust .....	.....	4159	.....	1888	
Beef (lean) .....	5313	1567	2250	664	70.5
Veal .....	4514	1314	1912	556	70.9
Ham (boiled) .....	4343	1980	1839	839	54.4
Mackerel .....	6064	1789	2568	758	70.5
Whiting .....	4520	904	1914	383	80.0
White of egg .....	4896	671	2074	284	86.3
Hard-boiled egg .....	6321	2383	2677	1009	62.3
Yolk of egg .....	6460	3423	2737	1449	47.0
Isinglass .....	4520	.....	1914	.....	
Milk .....	5093	662	2157	280	87.0
Carrots .....	3767	527	1595	223	86.0
Cabbage .....	3776	434	1599	184	88.5
Cocoa-nibs .....	.....	6873	.....	2911	
Beef fat .....	9069	.....	3841	.....	
Butter .....	.....	7264	.....	3077	
Cod-liver oil .....	.....	9107	.....	3857	
Lump sugar .....	.....	3348	.....	1418	
Commercial grape-sugar .....	.....	3277	.....	1388	
Bass's ale (alcohol reckoned) ..	3760	775	1599	328	88.4
Guinness's stout ..	6401	1076	2688	455	88.4

TABLE III.—Actual Energy developed by 1 gram of various articles of Food when oxidized in the Body.

Name of food.	Metrekilograms of force.	
	Dry.	Natural condition.
Cheshire cheese .....	2429	1816
Potatoes .....	1563	422
Apples .....	1516	273
Oatmeal .....	.....	1665
Flour .....	.....	1627
Pea-meal .....	.....	1598
Ground rice .....	.....	1591
Arrowroot .....	.....	1657
Bread crumb .....	1625	910
Lean of beef .....	2047	604



TABLE (continued).

Name of food.	Metrekilograms of force.	
	Dry.	Natural condition.
Lean of Veal .....	1704	496
Lean of ham (boiled) ...	1559	711
Mackerel .....	2315	683
Whiting .....	1675	335
White of egg .....	1781	244
Hard-boiled egg .....	2562	966
Yolk of egg .....	2641	1400
Gelatin .....	1550	
Milk .....	2046	266
Carrots .....	1574	220
Cabbage .....	1543	178
Cocoa-nibs .....		2902
Butter .....		3077
Beef fat .....	3841	
Cod-liver oil .....	3857	
Lump sugar .....		1418
Commercial grape-sugar .		1388
Bass's ale (bottled) .....	1559	328
Guinness's stout „	2688	455

TABLE IV.—Weight and Cost of various articles of Food required to be oxidized in the body in order to raise 140 lbs. to the height of 10,000 feet.

External Work = one-fifth of Actual Energy.

Name of food.	Weight in lbs. required.	Price per lb.	Cost.
		<i>s. d.</i>	<i>s. d.</i>
Cheshire cheese .....	1·156	0 10	0 11 $\frac{1}{2}$
Potatoes .....	5·068	0 1	0 5 $\frac{1}{4}$
Apples .....	7·815	0 1 $\frac{1}{2}$	0 11 $\frac{3}{4}$
Oatmeal .....	1·281	0 2 $\frac{3}{4}$	0 3 $\frac{1}{2}$
Flour .....	1·311	0 2 $\frac{3}{4}$	0 3 $\frac{1}{4}$
Pea-meal .....	1·335	0 3 $\frac{1}{4}$	0 4 $\frac{1}{2}$
Ground rice .....	1·341	0 4	0 5 $\frac{1}{2}$
Arrowroot .....	1·287	1 0	1 3 $\frac{1}{2}$
Bread .....	2 345	0 2	0 4 $\frac{1}{4}$
Lean beef .....	3·532	1 0	3 6 $\frac{1}{2}$
Lean veal .....	4·300	1 0	4 3 $\frac{1}{2}$
Lean ham (boiled).....	3·001	1 6	4 6
Mackerel .....	3·124	0 8	2 1
Whiting .....	6·369	1 4	9 4
White of egg .....	8·745	0 6	4 4 $\frac{1}{2}$
Hard-boiled egg .....	2·209	0 6 $\frac{1}{2}$	1 2 $\frac{1}{2}$
Isinglass .....	1·377	16 0	22 0 $\frac{1}{2}$
Milk .....	8·021	5 <i>d.</i> per qt.	1 3 $\frac{1}{2}$
Carrots .....	9·685	0 1 $\frac{1}{2}$	1 2 $\frac{1}{2}$
Cabbage .....	12·020	0 1	1 0 $\frac{1}{4}$
Cocoa-nibs .....	0·735	1 6	1 1 $\frac{1}{4}$
Butter .....	0·693	1 6	1 0 $\frac{1}{2}$
Beef fat .....	0·555	0 10	0 5 $\frac{1}{2}$
Cod-liver oil .....	0·553	3 6	1 11 $\frac{1}{4}$
Lump sugar .....	1·505	0 6	1 3
Commercial grape-sugar .	1·537	0 3 $\frac{1}{2}$	0 5 $\frac{1}{4}$
Bass's pale ale (bottled) .	9 bottles.	0 10	7 6
Guinness's stout „	6 $\frac{3}{4}$ „	0 10	5 7 $\frac{1}{2}$

TABLE V.—Weight of various articles of Food required to sustain Respiration and Circulation in the Body of an average Man during twenty-four hours.

Name of food.	Weight in ozs.	Name of food.	Weight in ozs.
Cheshire cheese .....	3.0	Whiting .....	16.8
Potatoes.....	13.4	White of egg .....	23.1
Apples.....	20.7	Hard-boiled egg.....	5.8
Oatmeal .....	3.4	Gelatin .....	3.6
Flour .....	3.5	Milk .....	21.2
Pea-meal.....	3.5	Carrots .....	25.6
Ground rice .....	3.6	Cabbage .....	31.8
Arrowroot .....	3.4	Cocoa-nibs .....	1.9
Bread .....	6.4	Butter .....	1.8
Lean beef .....	9.3	Cod-liver oil .....	1.5
Lean veal .....	11.4	Lump sugar .....	3.9
Lean ham (boiled).....	7.9	Commercial grape-sugar	4.0
Mackerel .....	8.3		

These results are fully borne out by experience in many instances. The food of the agricultural labourers in Lancashire contains a large proportion of fat. Besides the very fat bacon which constitutes their animal food proper, they consume large quantities of so-called apple dumplings, the chief portion of which consists of paste in which dripping and suet are large ingredients; in fact these dumplings frequently contain no fruit at all. Egg and bacon pies and potatoe pies are also very common *pièces de résistance* during harvest time, and whenever very hard work is required from the men. I well remember being profoundly impressed with the dinners of the navigators employed in the construction of the Lancaster and Preston Railway; they consisted of thick slices of bread surmounted with massive blocks of bacon in which mere streaks of lean were visible. These labourers doubtless find that from fat bacon they obtain at the minimum cost the actual energy required for their arduous work. The above Tables affirm the same thing. They show that .55 lb. fat will perform the work of 1.15 lb. cheese, 5 lbs. potatoes, 1.3 lb. of flour or pea-meal, or of  $3\frac{1}{2}$  lbs. of lean beef. Donders, in his admirable pamphlet 'On the Constituents of Food, and their relation to Muscular Work and Animal Heat,' mentions the observations of Dr. M. C. Verloren on the food of insects. The latter remarks, "many insects use, during a period in which very little muscular work is performed, food containing chiefly albuminous matter; on the contrary, at a time when the muscular work is very considerable, they live exclusively, or almost exclusively, on food free from nitrogen." He also mentions bees and butterflies as instances of insects performing enormous muscular

work, and subsisting upon a diet containing but the merest traces of nitrogen. The following conclusions may therefore be drawn from the foregoing experiments and considerations :—

1. A muscle is a machine for the conversion of potential energy into mechanical force.

2. The mechanical force of the muscles is derived chiefly, if not entirely, from the oxidation of matters contained in the blood, and not from the oxidation of the muscles themselves.

3. In man, the chief materials used for the production of muscular power are non-nitrogenous; but nitrogenous matters can also be employed for the same purpose, and hence the greatly increased evolution of nitrogen under the influence of a flesh diet, even with no increase of muscular exertion.

4. Like every other part of the body, the muscles are constantly being renewed; but this renewal is scarcely perceptibly more rapid during great muscular activity than during comparative quiescence.

5. After the supply of sufficient albuminoid matters in the food of man to provide for the necessary renewal of the tissues, the best materials for the production both of internal and external work are non-nitrogenous matters, such as oil, fat, sugar, starch, gum, &c.

6. The non-nitrogenous matters of food which find their way into the blood yield up all their potential energy as actual energy; the nitrogenous matters, on the other hand, leave the body with a portion (at least one-seventh) of their potential energy unexpended.

7. The transformation of potential energy into muscular power is necessarily accompanied by the production of heat within the body, even when the muscular power is exerted externally. This is doubtless the chief, and probably the only, source of animal heat.

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## XXV. *On a Problem in the Calculus of Variations.*

*By I. TODHUNTER, M.A., F.R.S.\**

IN the Philosophical Magazine for July 1866, Professor Challis has communicated some additional observations respecting the problem in the Calculus of Variations which had been discussed in various preceding Numbers of the Magazine. The problem may be thus enunciated: To determine the greatest solid of revolution, the surface of which is given, and which cuts the axis at two fixed points. I have stated in the Philosophical Magazine for June what I consider to be the solution of the pro-

\* Communicated by the Author.

blem as thus enunciated; and I think it will be admitted that this solution does give the solid of greatest volume, and is in harmony with the recognized principles of the Calculus of Variations.

In the Philosophical Magazine for July, a condition is attached to the enunciation, as will be seen from the following words which occur towards the beginning of the article:—"That a solid exists, the largest of all solids of revolution whose surfaces are of given area and extend *continuously* from one extremity of the axis to the other, there can, I think, be no reason to doubt. . . ." The result which is obtained is that the required solid is that which is generated by the revolution of a segment of a circle round its chord, the chord being the straight line which joins the two fixed points. This result is called the absolute maximum.

My present design is briefly to test the accuracy of this result, and the method by which it is obtained.

I may remark that the word *absolute* does not seem very appropriate, because it naturally suggests freedom from any restriction, whereas the result is only maintained with the restriction that the surfaces considered shall be *continuous*; but this is not a matter of great importance in connexion with my design.

I will first show, by examining a particular case, that the asserted result is erroneous.

The particular case I take is that in which the distance between the two fixed points is indefinitely small, so that, in other words, the generating curve is only required to meet the axis at one point. Then the assertion is that the solid of greatest volume with a given surface is that formed by the revolution of a circle round a tangent; on the contrary, I maintain that by taking an ellipse of very small excentricity, a solid can be formed of greater volume with an equal surface.

Let  $2a$  and  $2b$  be the axes of the ellipse, and let it revolve round the tangent at one end of the axis minor.

Then the volume generated is .

$$2\pi b \times \pi ab,$$

and the surface is

$$2\pi b \times 4a \int_0^{\frac{\pi}{2}} \sqrt{1 - e^2 \cos^2 \phi} \, d\phi,$$

where  $e$  is the excentricity.

Let  $r$  be the radius of a circle; then the corresponding volume and surface are  $2\pi^2 r^3$  and  $4\pi^2 r^2$  respectively.

Now I shall show that if the volumes of the two solids are



equal, the surface of the former solid is less than the surface of the latter; this is equivalent to the statement I have made above.

We have, by equating the volumes,

$$ab^2 = r^3,$$

that is,

$$a^3(1 - e^2) = r^3;$$

thus

$$a = r(1 - e^2)^{-\frac{1}{3}}.$$

Hence the surface formed by the revolving ellipse is

$$8\pi r^2(1 - e^2)^{-\frac{1}{3}} \int_0^{\frac{\pi}{2}} \sqrt{1 - e^2 \cos^2 \phi} \, d\phi;$$

and we have to show that this is less than  $4\pi^2 r^2$ ; that is, we have to show that

$$(1 - e^2)^{-\frac{1}{3}} \int_0^{\frac{\pi}{2}} \sqrt{1 - e^2 \cos^2 \phi} \, d\phi \text{ is less than } \frac{\pi}{2},$$

the excentricity  $e$  being supposed very small.

This may be shown in more than one way: the following will be sufficient. If  $e$  is very small, so that we may reject  $e^4$  and higher powers of  $e$ , the left-hand expression becomes

$$\left(1 + \frac{e^2}{6}\right) \frac{\pi}{2} \left(1 - \frac{e^2}{4}\right), \text{ or } \frac{\pi}{2} \left(1 - \frac{e^2}{12}\right).$$

This example is a special case of a general proposition which was enunciated in the *Philosophical Magazine* for March, and to which attention was again invited in July. The general proposition is the following: a ring having a circular transverse section is larger than any other ring having the same superficies, and the same radius either interior or exterior, but a different form of transverse section. Now I have just taken a special case of this general proposition, and shown that in this case the result is erroneous.

Moreover the general proposition itself is erroneous. For it may be shown in nearly the same manner that by taking, instead of the circle, an ellipse of very small excentricity with its major axis parallel to the axis of revolution, a solid can be formed of greater volume with an equal surface when the interior radius of the ring is given.

Again, the result which immediately follows in the *March Number* is also erroneous. A figure formed of a rectangle and a semicircle generates a solid which, under certain circumstances, is asserted to have the greatest volume with a given surface. It

will be found that by changing the semicircle into a semiellipse, a solid can be formed of greater volume with an equal surface.

In the first example which I brought forward, I supposed the length of the axis of the required solid of revolution to be indefinitely small, and I showed that the result which I am examining is incorrect. If the length of the axis be *finite*, it may be shown that, by changing the segment of a circle into a segment of an ellipse, a solid can in many cases be formed greater than that which is erroneously said to be the maximum, but having an equal surface. I do not say that this is possible in *all* cases; but the fact that it is possible in *any* case establishes the opinion which I am maintaining.

Of course I do not assert that in the cases I have noticed I have here assigned the greatest solid, or a maximum solid; I have only professed to show that the statements on which I am commenting are erroneous.

The foregoing examples will enable a person who has not studied the Calculus of Variations, but is acquainted with the elements of the Differential and Integral Calculus, to form an opinion on the subject I am discussing. I shall proceed, in the second place, to show that the method by which the erroneous results are obtained is essentially unsound.

Let

$$u = \int v dx,$$

where  $v$  is a function of  $x, y$ , and the differential coefficients of  $y$  with respect to  $x$ . Then by the Calculus of Variations we obtain

$$\delta u = \int A(\delta y - p \delta x) dx + B,$$

where  $B$  stands for certain terms which are free from the integral sign, and  $A$  is a function of  $x, y$ , and the differential coefficients.

Now if  $u$  is to be a maximum or minimum, we must have, according to the received theory,  $A=0$ ; and this is admitted in the article in the July Number. And if there are more than one value of the ordinate corresponding to a given abscissa, the relation  $A=0$  must in general be satisfied at each point thus assigned.

Suppose that  $y'$  and  $y''$  represent two values of  $y$  which correspond to one abscissa  $x$ ; and let  $A'$  and  $A''$  denote the corresponding values of  $A$ . Then we must have  $A'=0$  and  $A''=0$ . This is also admitted in the article in the July Number; the equations  $A'=0$  and  $A''=0$  are expressed at full on page 52. Then from these the equation  $A'-A''=0$  is deduced, and the following words are added:—"This last equation, inasmuch as it takes account of both values of  $A$ , is the one which the form of the curve is required to satisfy. To draw any inference from

one value of  $A$  and exclude the other would be nothing short of error."

I admit of course that the equation  $A' - A'' = 0$  must be satisfied; but I do not admit that this is *the one* equation which the form of the curve is required to satisfy.

We have to satisfy *both*  $A' = 0$  and  $A'' = 0$ . We may of course try to assist ourselves by discussing the equation  $A' - A'' = 0$ ; but any result which we deduce from the last equation will not be applicable to the problem we are solving, unless it makes *both*  $A' = 0$  and  $A'' = 0$ . It is therefore unnecessary to examine the validity of the process which is applied to the equation  $A' - A'' = 0$ , so long as it is obvious that the result does not make both  $A' = 0$  and  $A'' = 0$ .

That the equations  $A' = 0$  and  $A'' = 0$  are not satisfied when we take for the required curve a segment of a circle, can be immediately ascertained by trial.

Or we may establish this assertion by referring the curve to polar coordinates. In this case we shall have only *one* value of  $r$ , corresponding to *one* value of  $\theta$ ; so that we have no occasion to consider two values of  $A$ . The differential equation in polar coordinates, as given in the Magazine for March, is

$$\frac{r \sin \theta (r + r'')}{(r^2 + r'^2)^{\frac{3}{2}}} + \frac{r' \cos \theta - 3r \sin \theta}{r(r^2 + r'^2)^{\frac{1}{2}}} = \frac{\sin \theta}{\lambda},$$

where accents denote differential coefficients. Now the equation corresponding to a segment of a circle is  $r = C_1 \cos(\theta - C_2)$ , where  $C_1$  and  $C_2$  are constants. It will be found immediately, on trial, that so long as  $C_2$  is not zero the equation is *not* satisfied, whatever sign we give to the radical.

Thus it follows that the method which I am examining is opposed to the fundamental principles of the Calculus of Variations.

I wish to advert to one of the results enunciated in March, because I am uncertain whether it is still maintained, or is abandoned as erroneous. The result was enunciated thus:—"The solid consisting of a cylinder and two hemispherical ends of the same radius, is larger than any other solid of revolution having the same amount of surface and the same length of axis."

I urged two objections against this, one of them being that the fundamental equation  $A = 0$  is not satisfied. I cannot agree with Professor Challis that he sufficiently meets the objection. It seems to me that there are only three ways in which the objection may be combated: (1) by showing that the equation  $A = 0$  is satisfied; (2) by denying that it is necessary to satisfy the equation  $A = 0$ ; (3) by showing that although it is in general necessary to satisfy the equation  $A = 0$ , yet there are special reasons which remove the necessity in the present case.

But the objection is not removed by reasoning which does not bear on these points: it is not removed, for example, by showing that the proposed solution satisfies  $\Lambda=0$  at some points, and satisfies  $p=0$  at all the other points.

It is almost superfluous to advance another argument against the untenable result; but I may just mention that, by changing the hemispherical ends into semispheroids, we can form a solid having the same surface and the same length of axis as that which is erroneously called the greatest, but having a greater volume.

Having shown by examples and by theory that the results given in the Numbers for March and for July are inadmissible, I shall proceed in the third place to offer some remarks as to the possibility of solving the problem with the condition of *continuity*.

The word *continuous* may have more than one meaning; but I think that the following remarks will apply with any meaning which is likely to be assigned.

The figure which by its revolution round the axis generates the solid of *greatest* volume with a given surface, is a figure formed of an arc of a semicircle and a straight line which coincides in direction with the bounding diameter. This figure will be regarded as non-continuous by those who seek for a continuous solution. But we know that we can in general draw a continuous curve through any assigned number of points, however large. Hence we can in effect make a continuous curve coincide as nearly as we please with the non-continuous curve which gives the greatest solid. The best method of conceiving this to be done is to employ the theorems which serve as the foundation for the expansion of functions in terms of sines and cosines of multiple angles.

It seems to follow from this consideration that it is in vain to seek for any solution, continuous or non-continuous, which differs from that determined by the semicircle and straight line.

Again, whether a solution be continuous or non-continuous, it must satisfy the fundamental equation of the Calculus of Variations which I have denoted by  $\Lambda=0$ ; and it does not seem possible to satisfy this equation except in the manner indicated in the Magazine for June.

The very interesting investigation respecting the course of a ship, to which Professor Challis refers, was unknown to me when I published my 'History of the Calculus of Variations.' I regret this, because the subject of discontinuous solutions of problems in the Calculus of Variations appears to me important; I have given several examples, and I should have been glad to have included in my work a notice of every case which had been discussed. I venture to suggest, without, however, laying much



stress on the suggestion, that if there are reasons for asserting that the problem of the greatest solid of revolution ought to have a *continuous* solution, there will also be reasons for making a similar assertion for the problem respecting the course of a ship.

I will advert to one fact which, although not essential, will be of use in studying what has been written on the problem under discussion.

I have quoted above the ordinary formula

$$\delta u = \int A(\delta y - p\delta x)dx + B$$

as that which will probably be most familiar to readers of the Magazine. It has, however, been shown by some of the most eminent writers on the subject, that we may use the formula

$$\delta u = \int A\delta y dx + B;$$

A is the same in the two formulæ, but B is not. I retain the opinion that I have elsewhere expressed in favour of the second formula: it seems to me to be obtained in a more simple and intelligible manner than the first, and to be better adapted to the higher investigations by which we discriminate between a maximum and a minimum.

Although I do not admit that the articles in the Magazine for March and for July have contributed directly to the solution of the problem discussed, yet I am glad that attention has been again drawn to the subject. My own conviction is that the problem is no longer perplexing, but that its true solution is that which was stated and supported in the Magazine for June.

Cambridge, August 2, 1866.

## XXVI. *On Molecular Physics.* By Prof. W. A. NORTON\*.

[Continued from vol. xxxi. p. 282.]

**M**AGNETIC Condition of the Sun.—The intimate magnetic relation subsisting between the earth and sun enforce, even in the present general exposition of terrestrial magnetism, a brief consideration of the probable magnetic condition of the sun. We have seen that the sun's surface must be traversed by magnetic currents developed in two ways,—(1) by reason of the sun's rotation about an axis; (2) by reason of the combined effect of its motion of rotation and its motion of translation through space (vol. xxxi. p. 280). According to the most reliable determinations the sun's progressive motion is directed toward a point whose longitude is  $253^{\circ} 16'$ , and north latitude  $57^{\circ} 27'$ , and with a velocity of  $4\frac{2}{3}$  miles per second, while his velocity of rotation at the equator is 1.3 mile per second. Accordingly the currents developed from the second cause must originate at the parts of

\* From Silliman's Journal for March 1866.

the sun's surface that have a heliocentric longitude of about  $163^{\circ}$ , and with a gradually decreasing intensity on both sides of that point. The north pole of this system of currents, as developed at any moment of time, will lie in the heliocentric latitude  $33^{\circ}$ , and longitude  $73^{\circ}$ . In the course of one complete rotation of the sun (25 days), this pole will be carried around the parallel of latitude which contains that point. The resultant of the currents thus developed that will traverse any locality at the end of one or more rotations will therefore run parallel, or nearly so, to the equator, like the currents that originate in the simple rotation. In all this we neglect the small inclination of the sun's equator to the ecliptic (about  $7^{\circ}$ ); or suppose the equator and ecliptic to coincide. It appears, therefore, that the poles of all the permanent currents should coincide with the poles of rotation.

But it is important to observe that at every moment of time there will be, coexisting with the permanent currents, a system of new currents originating as above mentioned; and that therefore there will be a *secondary magnetic equator*, crossing the ecliptic in  $163^{\circ}$  and  $343^{\circ}$  of longitude, and a *secondary magnetic pole*, in longitude  $73^{\circ}$  and north latitude  $33^{\circ}$ . Or rather the nodes and pole should be somewhat to the east of these positions, since the currents developed must decline gradually and the rotation carry them forward. The individual parallel currents of this system must decrease in intensity in both directions from their equator, by reason of the increasing distance from the equator of rotation of the points of tangential action of the impulses of the æther and cosmical matter, and the decreasing size of the magnetic parallels followed by the currents. It will be readily seen, in view of the fact that the sun derives its magnetism in part from its motion toward a point in the northern celestial hemisphere, that the magnetic intensity of its northern must be greater than that of its southern hemisphere.

*Origin of the Sun's Spots.*—The systematic observations upon the sun's spots made by Carrington, Schwabe, Wolf, Secchi, and others, and especially the detailed discussion to which all the observations have been subjected by Professor Wolf, have served conclusively to establish that the sun's spots have their immediate origin in some action of the planets Jupiter, Saturn, Venus, and the Earth upon the photosphere of the sun, or in such action cooperating with some other cause. (See *Astronomische Nachrichten*, Nos. 839, 1043, 1091, 1137, 1150, 1160, 1173, 1181, 1185, 1223, 1234, 1270, 1289, 1294, 1355, 1526, &c.)

Professor Wolf has determined the epochs of maxima of the sun's spots for a period comprising 100 years; and finds that the period of the spots varies from 8 to 16 years, and that its

mean value is 11.15 years. He gives a formula for determining the spot-condition of the sun at different dates, in which the several terms represent the specific actions of the four planets just mentioned, dependent upon their masses, distances, and annual motions, and which gives results in close correspondence with the results of the observations made between 1826 and 1848 (*Astronomische Nachrichten*, No 1181). He has more recently extended his investigations so as to include, but with less certainty, a much longer period.

The epochs of maxima and minima from 1750 to 1856 are given in the following Table, to which we have added the corresponding mean heliocentric longitudes of Jupiter and Saturn, the two planets upon which the varying number of spots developed during a year chiefly depend.

Epochs of maxima.	Jupiter.	Saturn.	Epochs of minima.	Jupiter.	Saturn.
1750.0	4.42	231.6	1755.7	177.4	301.4
1761.5	353.4	12.2	1766.5	145.1	73.5
1770.0	251.4	116.2	1775.8	67.4	187.3
1779.5	179.7	232.4	1784.8	340.5	297.3
1788.5	92.8	342.4	1798.5	36.3	104.9
1804.0	203.3	172.0	1810.5	40.5	251.5
1816.8	231.8	328.5	1823.2	66.0	46.8
1829.5	257.2	123.9	1833.8	27.7	176.4
1837.2	130.9	218.0	1844.0	337.3	301.2
1848.6	116.9	357.5	1856.2	347.6	90.4

It will be seen that (omitting the results answering to the first two epochs of the Table, which will be separately considered) at the epochs of maxima Jupiter was in some position intermediate between the point toward which the progressive motion of the sun is directed (long.  $253^{\circ}$ ) and the diametrically opposite point (long.  $73^{\circ}$ , which is the longitude of the secondary magnetic pole), reckoning from east to west from the first point to the second. The average position is  $183^{\circ}$ , or *in the vicinity of the descending node of the currents of the secondary magnetic equator* (p. 206). Again, omitting the epochs 1755.7 and 1766.5, at all the epochs of minima the positions of Jupiter fell in the other half of the ecliptic, and his average position was in long  $23^{\circ}$ . This is in the vicinity of the *ascending node* of the same equator, which lies somewhat to the east of  $343^{\circ}$  (p. 206). If we consider now the case of Saturn, we find that his average position at the epochs of minima was  $182^{\circ}$ , or  $183^{\circ}$  if we take the first two epochs into account. If we separate the positions that fall in the two halves of the ecliptic, lying on opposite sides of the line from  $253^{\circ}$  to  $73^{\circ}$ , we obtain the average positions  $162^{\circ}$  and  $333^{\circ}$ . If we include the first two epochs, the latter average



becomes  $348^{\circ}$ . The average position of Saturn at the epochs of maxima was  $236^{\circ}$ .

If we now direct our attention to the first two epochs of maxima, we shall perceive that Jupiter was in that part of the ecliptic in which his ordinary action is the least; and if we refer to the first two epochs of minima, it will be seen that he was in or near the part of the ecliptic in which his ordinary action is the greatest. We must conclude, then, that from 1750 to 1766 the normal condition of things at the two nodes was greatly changed, and that the action of Saturn conspired with that of Jupiter to produce the anomalous results.

In view of the general results that have now been obtained, we may infer (1) that in general the action of a planet to produce spots is greatest in the portion of the ecliptic which contains the descending node of the secondary magnetic equator, and least in the opposite portion; (2) that the action is approximately the same at corresponding points on one side and on the other of either node. But the indications are that a somewhat greater liability to epochs of maxima exists when the planet is on the side of the line of the magnetic nodes toward which the progressive motion of the sun is directed than on the opposite side. This is most observable in the case of Saturn; for his average position at the epochs of maxima was  $236^{\circ}$ , while that of Jupiter was  $183^{\circ}$ .

By an examination in detail of the diverse positions of the operating planets at all the different epochs, and following their motions from one epoch to another, it may further be shown (1) that a planet operates more effectively before and after it has passed either magnetic node than at the very node; (2) that the normal positions of the two nodes are not far from  $0^{\circ}$  and  $180^{\circ}$  of longitude, the sun's rotation having the effect to displace them about  $17^{\circ}$  toward the east (p. 206); (3) that the principal maxima of planetary action occur at about the positions  $135^{\circ}$  and  $230^{\circ}$  on opposite sides of the descending node, and that under certain circumstances other positions of inferior maxima manifest themselves, lying in the vicinity and on opposite sides of the ascending node; (4) that the principal minimum falls at about  $0^{\circ}$ , or at the ascending node, and a secondary minimum at  $180^{\circ}$  (or the descending node); but in the normal state of things the effect of the planet appears to experience small changes in the space from  $320^{\circ}$  to  $70^{\circ}$ . These positions of maxima and minima are given here only as first approximations.

These results of observation, deducible for the most part from the Table we have given (p. 207), and confirmed by a detailed examination of Professor Wolf's entire series of determinations, are all decided intimations of a dependence of the sun's spots



upon the varying magnetic or electric condition of the sun, and indicate that they are closely connected with the varying intensity of the magnetizing or demagnetizing action of the system of secondary magnetic currents developed by the sun's progressive motion, in conjunction with the cooperative action of the electric waves that proceed from the region (long.  $253^{\circ}$  and lat.  $57^{\circ}$ ) upon which the impulses of the æther and cosmical matter fall normally. Of these two operative causes, the first should augment on both sides of the secondary magnetic equator, and for considerable distances. It should be much greater on the side of the descending than on that of the ascending node of this equator, because the new magnetic currents originate on the former side. The electric currents developed at any instant upon the ascending-node side of the sun run in the opposite direction, and tend to weaken the prevailing currents. The residual excess of the latter over the former at any point, and at any instant, constitutes the new effective magnetic current at that point and moment of time (*l. c.* p. 266). Each of these two sets of currents may also play a certain part in conjunction with the magnetic currents that result from them. It will be seen, then, that the results of observation which we have signalized (pp. 207–208) are, in general, such as should ensue if the operative causes here considered cooperate with some action of the planets to develop the spots, each tending to enhance the effect of the other.

The tendency of the second operative cause, if it conspires in this manner with the planetary action, should be to make that action apparently the greatest when the planet is about in long.  $253^{\circ}$ ; and therefore the region of the spots developed by the planet (which lies near the ecliptic on the side of the sun turned toward the planet) is nearest the central point of origination of the waves in question. On the other hand, the tendency of the same general cause should be to make the effect of the planet least at the diametrically opposite point (long.  $73^{\circ}$ ).

It may be seen that if the three causes here supposed to be continually in operation—and to be cooperating more or less according to the positions of the planets with respect to the special points of maxima and minima alluded to, at the same time that the individual planets are conspiring more or less with each other according to their relative positions—should determine spots by their conjoint action; their effects, in respect to the connexion of the epochs of maxima and minima with certain positions of the planets, and the lengths of the periods comprised between these epochs should correspond, in the main, with the results of observation.

From the point of view we have now reached we may gain an  
*Phil. Mag.* S. 4. Vol. 32. No. 215. Sept. 1866. P

insight into the probable nature of the process of origination of the sun's spots. Conceiving the luminous matter of the sun's photosphere to be endued with the properties we have recognized in those emanations of solar matter that enter the earth's photosphere (*l. c.* pp. 275–280), we may regard it as inductively magnetized by the sun's magnetic currents, and disposed in the lines of magnetic polarization, and probably also distributed into separate masses having in the various latitudes all the diverse directions of the sun's directive force. We have reason to suppose that in the upper portions of such masses the molecules on each line of polarization will be so widely separated as to be subject to an effective force of molecular repulsion from the sun (*l. c.* p. 272), and that in the state of equilibrium this is neutralized by the magnetic attraction between contiguous molecules. Now such a state of equilibrium may be disturbed, and the matter expelled to an indefinite distance in three ways,—(1) by demagnetization; (2) by electric discharges along the lines of polarization; (3) by both of these causes operating together. A demagnetization may result, as we have seen, from the new currents developed in the upper photosphere by the tangential action of the æther and cosmical matter; and electric discharges may ensue in consequence of the propagation of electric waves in every direction from the region (in long.  $253^{\circ}$ , and N. lat.  $57^{\circ}$ ) that receives the impulses from the æther and cosmical matter normally. The points of greatest and least demagnetization should be such as have been already indicated (p. 209). But the photospheric matter should also be subject to the molecular repulsion of the masses of the different planets; and one effect of the impulses of this force should be to develop electric waves or currents proceeding from the region normally exposed to them. Such waves are of the same character, and originate essentially in the same manner as the “radial currents” that we have recognized as playing a conspicuous part in terrestrial magnetic phenomena (*l. c.* pp. 271–272). They should be most energetic, as in the case of these radial currents, at a certain moderate distance from the point directly under the planet, *i. e.* in low latitudes. On the other hand, it is to be observed that for a certain distance from this point the repulsive force of the planet may check the expulsion of the solar matter by its direct action.

The tendency to the formation of spots should be wanting at the permanent magnetic equator (or rotation equator), because the lines of polarization are there parallel to the surface and the induced magnetism feeble. Again, the effect of demagnetization should be greatest in low latitudes, where the total magnetic intensity is the least, and where also the new demagnetizing cur-

rents are most energetic. To this we may add, that as we have reason to believe that the temperature of the *mass* of the sun decreases toward the poles (*l. c.* pp. 269–270), the molecules of the photospheric matter may be less widely separated there, or be combined in groups so as to be subject to a less energetic force of repulsion from the sun. It is conceivable, too, that in special localities the electric waves or currents originated by the planets may operate to disunite molecules in the act of combining or condensing at the surface of the photosphere (the state of things supposed by Faye), and so bring them into the condition to be repelled and completely dispersed by the repulsive force of the sun. The process of dispersion having once begun, from any cause, may extend indefinitely downward.

There is a special mode of origination of spots, connected with the sun's motion in space, that has not yet been noticed. It is that the cosmical matter as it flows away from the region of normal impact toward the equator will become demagnetized, and thus initiate the process of dispersion of certain portions of the photospheric matter. The effect will be especially produced on the opposite side of the pole from the point of normal impact, as the changes of the induced magnetism will there be the greatest. A similar effect may ensue from a flow toward the equator of the matter at the very surface of the photosphere, produced by the impulses of the cosmical matter or æther. The phenomena are precisely similar to the auroral phenomena that light up occasionally the earth's photosphere (*l. c.* p. 280). This is undoubtedly the origin of the annual maximum of spots after the autumnal equinox detected by Professor Wolf. It is the result of the effects previously noticed, augmented by that here considered. An inferior maximum manifests itself in December, which is the direct result of this cause alone. (See *Astronomische Nachrichten*, Nos. 1043 and 1223.) It is important to observe here that when a planet is on that side of the sun, or in the vicinity of the ascending magnetic node before alluded to, it tends to check this southerly flow of matter at the surface of the photosphere, and so prevent the development of spots from the cause in question. We may add that we have doubtless another revelation of its operation in the predominating irregular disturbances of the magnetic needle in the autumnal months (or from August to December inclusive; see Professor Bache's Reports). The secondary maximum of the annual inequality of spots and magnetic disturbances near the vernal equinox is to be chiefly attributed to the demagnetization in the vicinity of the descending magnetic node already considered.

The spots are more numerous in the northern than in the southern hemisphere of the sun, because the low latitudes at



which they chiefly originate lie, in the northern hemisphere, nearest the region (long.  $253^{\circ}$ , N. lat.  $57^{\circ}$ ) from which the electric and material currents radiate, and because in the northern hemisphere alone is the flow of the material currents in the direction to be attended with a demagnetization. Again, the spots are confined to a narrower belt in the northern than in the southern hemisphere, because, the magnetic intensity of the northern hemisphere being the greatest (p. 206), the ordinary limiting parallel of the spots (which is the circle at which the demagnetizing action from either of the two causes specified, together with the electric discharges along the photospheric columns, cease to be sufficient to effect the dispersion of these columns) must lie nearest the equator in that hemisphere.

It is to be observed that spots may arise from electric discharges along the photospheric lines of polarization, although no demagnetizing action may come into operation; and it is even possible that indirectly an increase of magnetic intensity may, in special cases, cooperate with such currents.

*Note.*—Since the foregoing was written, the line of investigation here entered upon has been followed up, and new and important general results obtained. One of the principal results is, that the *density or quantity of matter of the sun's photosphere, in the region of the spots, experiences periodical augmentations*, in consequence of certain effects produced by Jupiter and Saturn while passing by the first quadrant of heliocentric longitude and the sun's north magnetic pole, and that these augmentations of density, in connexion with the subsequent diminutions, are one of the determining causes of the great variations that occur in the length of the period of the sun's spots (viz. from eight to sixteen years). Another cooperative cause consists in the diverse positions of the planets, *especially of Venus*, with respect to positions of favourable action, at the epochs of heliocentric conjunction with the earth. The other causes have been intimated.

[To be continued.]

XXVII. *Optics of Photography.*—On a new Process for Equalizing the Definition of all the Planes of a Solid Figure represented in a Photographic Picture. By A. CLAUDET, F.R.S.\*

ONE of the greatest deficiencies of photography in the representation of solid figures is the impossibility of obtaining a well-defined image of all the various parts situated on different planes; for it is well known that the best object-glasses can give a sharp image only for the plane in focus; the images of the objects situated before and behind are more and more confused as they are more and more distant from that plane.

\* Communicated by the Author, having been read at the British Association, Nottingham Meeting, 1866.



To obviate this, or rather to equalize the effect to a certain degree, it is customary to reduce as much as possible, by means of diaphragms, the aperture of the lens. The object of such diaphragms is to cut off all the oblique rays, and to employ only the rays which emerge from the lens at the least angle possible. It is evident that when the rays are emerging from the centre of the lens, they follow a course so nearly parallel that any equal points of the object on various planes are included between spaces not varying much in size; so that although these points are distant from the plane which is represented at the mathematical focus with the greatest definition, they form their image within a circle of confusion so near the circle of definition that the eye cannot easily detect the difference, and the image of the solid figure appears well defined in its various planes.

But this result cannot be obtained without sacrificing a great amount of the light which falls on the lens and is stopped by the diaphragm; consequently the time of exposure for the formation of the image is to be increased as much as the surface of the lens has been reduced. It is then obvious that, in the case of portrait-taking, the advantage which would be gained in point of definition is lost by the unavoidable unsteadiness of the sitter, and at all events is more than counterbalanced by the constrained expression resulting from a long sitting.

Even supposing that the person could sit sufficiently long without moving, and preserve all the while the same expression, it is a question not difficult to decide in an artistical point of view, whether a photographic portrait showing all the pores and asperities of the skin, with the smallest of its wrinkles, would ever be an agreeable or artistic production.

Excessive minuteness is the greatest reproach which has been made by artists to the best photographic portraiture; and in order to obviate it, some have gone so far as to suggest that it would be desirable that photographers should take their portraits *a little out of focus*. But these artists, forgetting certain laws of optics, failed to observe that it was impossible to represent the whole of the figure in *the same degree* out of focus. If, for example, the nose was a little out of focus, the eyes would be considerably more so, and the ear still more; in fact some parts of the figure would be quite indistinct and confused, whilst one part only would be a little softened down by a slight deviation from the plane of sharp focus.

Although such a method is therefore unavailable, this suggestion, being made in a true spirit of progress, was worthy of consideration; and a very useful lesson was to be learned from the well-meant recommendation that photographic portraits, to be agreeable and artistic in effect, should not partake too much of the mathe-

mathematical truth which is inherent to the action of the most perfect lenses, and which is particularly observable in the part of the image situated in the plane of the exact focus of the lens.

Convinced myself of the advantage which, in an artistical point of view, would result from photographic portraits being taken in such a manner that they should as much as possible resemble a work of art, in which all the features are marked by light touches of the brush or pencil, softly blending from light to shade, such an important subject has for a long time occupied my attention. My precise object has been to discover a method of removing, if possible, from photographic portraiture that mechanical harshness which is due to the action of the most perfect lenses.

In the best works of art all the effects are produced by a soft and harmonious treatment; nothing is hard or dry, nothing is too minutely delineated: in fact the hand of the artist is not capable of microscopic correctness—and fortunately so, for its work is not intended to be examined by a magnifying lens; still the general effect may be sufficiently minute for the artistic purpose.

Notwithstanding its defects, photography is the great teacher to artists: they find in it the true reflex of nature; it shows the correct distribution of light and shade with all its delicate half tints; its perspective drawings are perfect, and it represents the folds and texture of draperies in the most exquisite manner. But if art derives a great advantage from the imitation of photographic productions, art is in its turn a very competent and valuable teacher of photographers. Their works indeed have no value if they do not partake of a certain character which distinguishes the best works of art. And therefore photographers must not despise the recommendations of true artists; for in trying to imitate art they will often improve their own productions. Therefore as artists have nothing better to do than to imitate photography, so photography has nothing better to do than to be guided by art.

By the laws which regulate the action of lenses, it happens, as has been already pointed out, that in the representation of a solid figure there is strictly only one plane of that solid which can be taken in perfect focus. The image therefore of that plane is not in harmony with the images of the other planes, which are not so sharply defined. This inequality in the texture of the image cannot but be considered a defect; and it would be a great advantage if it were possible to equalize the effect, even at the cost of losing the mathematical accuracy of the plane in focus. I hope to show indeed that such a loss would be really a considerable gain. If photographic portraits should not exhibit all the pores, wrinkles, and defects of the skin, it is still less desi-

able that only one part of the face should be in that condition, while all the others should gradually lose their sharpness as they are more and more distant from the plane of definition.

We can at will bring the focus upon any plane of the figure. In taking portraits not smaller than miniature size, we may choose the nose, the eyes, or the ears; but we cannot have the three equally sharply defined; and photographers endeavour to focus upon a middle plane, for example upon the eyes, in order to have the nose and the ears in the same degree of less perfect definition, not very far from that of the eyes.

Perfection in the portrait would be attained, were it possible to do so, first by taking the image of the nose, then, after having altered the focus, the image of the eyes, and finally, after again altering the focus, the image of the ear, and then, from these various images, forming a collective portrait. Such an idea may appear impracticable, possibly even absurd, and it is sure on first thoughts to be rejected and condemned. Yet I seriously, and after mature consideration both of the practice and of the theory of such a scheme, propose its adoption as one of the greatest improvements which will have been introduced in photography since its discovery. I beg to be allowed to explain the method in which I conceive I have solved the difficulty I have above alluded to.

Let me premise a few words upon the effect produced by the experiment of taking the photographic image of the focimeter. This instrument, I may be permitted to remark, was invented by me upwards of twenty years ago, and has been constantly used in my operating-room in order to test in what degree the chemical and visual foci of lenses coincided or differed. Until it came into use, nobody had ever dreamt that they did not exist in the same plane when the object-glasses were as much achromatic as those of the best telescopes. This fact being demonstrated by the instrument I refer to, was the cause of a complete change in the construction of lenses for photographic purposes; and from that time opticians have endeavoured to calculate, and succeeded in discovering curvatures the combination of which, to invent a phrase, achromatize, with the visible rays of light, the invisible rays which are exclusively endowed with the chemical action. The use of the focimeter I have found indispensable since the further discovery I have made that the two foci undergo continual changes from various atmospheric influences; and no photographic studio, therefore, should be without this instrument; for no optical combination is capable of preserving an invariable coincidence of foci, and the photographer must have the means at any moment of testing the then state of the elements, and of the light itself, in order to ascertain any change in its refraction and to act accordingly.



My focimeter, a model of which is on the table, is made of eight separate segments of a disk, mounted spirally on a horizontal axis of 12 inches, corresponding with the optical axis of the lens; the segments are all separated and distant about  $1\frac{1}{2}$  inch from each other. In a front view they form on the ground glass the image of a complete and regular disk. The segments are covered with some uniform and well-defined devices; and the centre of each is marked with its number, from 1 to 8. The first segment is the nearest, and the last the furthest from the lens.

By moving slightly and slowly forward and backward the focusing or ground glass, any one of these segments, and all in succession, may be brought into focus. If we focus upon No. 4, for example, we see that the segments before and behind gradually lose their sharpness, in a greater or less degree, according to the quality of the lens; and from that experiment we may judge of what is empirically called the depth of focus of the lens. By comparing at the same time the photographic image with the image we had on the ground glass, we see if the visual and chemical foci agree, or to what extent they differ. But our present object not being to test whether the chemical and visual foci agree, we will take a lens in which we know that they coincide.

Now, supposing that we focus upon No. 1, we shall find that the photographic image of that segment will be very well defined, No. 2 a little less, No. 3 and all the others until No. 8 gradually losing their sharpness, so that No. 8 will be the most indistinct. In the same way, if we take a portrait so that the nose is on the plane of No. 1, this part of the face will be well defined; the eyes, which are on the plane of No. 2, will be a little less well defined; the ear, on the plane of No. 3, still less defined; and if the body is obliquely turned, the shoulder, which corresponds with the plane of No. 8, will be considerably confused.

Experimenting again upon the focimeter, let us suppose that, after having operated with No. 1 in focus, we move the frame holding the plate to a point previously marked on the camera-board where No. 8 is in perfect focus. If we then expose the plate a second time, or rather continue the exposure, we shall find that upon the first confused image of No. 8 a new image well defined has been impressed, and at the same time a confused image of No. 1 will have been impressed upon the first image of No. 1 which was well defined.

In examining the result, we shall find it better than if the second impression on both segments, No. 1 and No. 8, had not been taken. In the middle of a confused image of No. 1 and No. 8 we shall have one perfectly defined, the whole having the appearance of the shadow of a pin not quite in contact with the surface; that shadow being slightly blended from dark to light,



but still sufficiently defined to show the exact form and size of the pin.

Now what has been done for the two extreme segments of the focimeter Nos. 1 and 8, can consecutively be done for the intermediate segments Nos. 2, 3, 4, 5, 6, 7, and 8; and in fact it is unavoidably done during the movement of the plate from No. 1 to No. 8; and the result is that every segment has the image of any small spot delineated upon it as if that spot was seen through a thin vapour.

This being well understood, let us apply the same mode of operating to the taking of a portrait; and while the person is sitting, let us move the frame holding the plate from the point of the focus of the nose to the focus of the furthest point of the figure. It is evident that during the movement of the plate the various planes of the figure will have been consecutively *in focus* and *out of focus* during one part of the exposure, and all in the same degree. Thus we have by a very simple contrivance found the means to realize the wish of true artists, viz. to take a photographic portrait without hard lines, but with the light and shades blended in the most artistic harmony.

We now arrive at the most important part of the discovery. The result may be obtained in greater perfection without having to move the frame holding the plate in order to adapt it consecutively to the focus of each of the planes of the figure. In moving the frame, it is evident that in one direction we increase, and in the other we reduce the size of those parts of the image which are consecutively brought into focus. The result is to exhibit more conspicuously than when these parts were out of focus the exaggeration of perspective which is inherent to all photographic representations taken by lenses not very distant from the figure—an exaggeration, I may remark, so disagreeably apparent in all large portraits taken by too short-focus lenses. To obviate this increase or reduction of the size of the image of the various planes of the figure, it would be necessary, if this were practicable, during the operation to change the lens and rapidly to substitute another having a focus appropriate to the distance of the new plane without altering the distance of the plate, so that the plate should not have to be moved forward or backward for the adaptation of the various foci according to each distance of plane.

It happens fortunately that this change of foci may be effected with the same object-glass when that object-glass is a double combination of lenses. The focus and power of such double combination being the result of the distance which separates the two lenses, it may be increased or reduced merely by altering that distance. Now if during the operation we bring nearer or further the two lenses, by this simple means we adapt the

focus of every plane to the immoveable frame holding the plate ; and we are enabled thus to represent consecutively on the plate an image of every plane, with a less reduction or increase of size than when the power of the double combination remains the same ; for it happens fortunately that, to reduce the focus, we must separate the lenses, by which the power is increased. The alteration of the distance which separates the two lenses is effected by a rack and pinion acting upon a tube containing the back lens, that tube sliding into another containing the front lens, which remains fixed during the adaptation of the focus to the distance of every plane by means of a gradual movement communicated to the back lens during the sitting. The inspection of the apparatus, which I submit to the Meeting, will enable any visitor interested in the question to understand its action.

It is marvellous when we reflect that there is nothing to wish for in the shape of contrivances having for their object the perception of vision, and that from time to time man invents, or thinks he invents, what nature had done in the most perfect manner. The eye is supplied with a lens in the same way as the camera obscura ; the retina is the screen on which, like the ground glass of the camera, the light reflected by all the natural objects form their image. By various humours through which the light is refracted, the spherical aberration is corrected and the most perfect achromatism is produced ; the eye is endowed with muscles which enable it to alter the focal distance of the lens according to the various distances of the objects. Optics is able to imitate all these beautiful contrivances except the last, which is available only on account of the way in which we exercise the perception of vision. We see at once only a very small part of the image—that part which is projected on the centre of the retina ; and the eye can adapt its focus to the distance of that part, and, as rapidly as thought, when directing its attention to another part it adapts its focus to that new distance. Therefore it matters not whether the other parts are in focus ; we have only the perception of what we want to see, and, by the proper adaptation, that sensation conveys to our mind only a well-defined image. It cannot be so with the camera obscura, because, the photographic image produced by it being at once permanently fixed entire by the same exposure, we cannot change it in changing the focus ; the only thing we can do is to impress a stronger image on a fainter image. The artificial optical instrument being destitute of a self-acting changing adaptation to the focus of all the other planes, can represent only one plane *in focus* ; but if it had that adaptation, the surface receiving the impression of the image in a permanent manner (not like the retina, which does not retain the impression), that impression would consist of a number of

images superposed one upon another. For this reason nobody would ever have thought of proposing to employ a lens which, moving during the exposure, would adapt itself consecutively to the foci of all the other planes of the image. But from the fact that the eye can easily and usefully alter its focus according to the distance of the plane it wants to examine, and unconsciously discard the image of the other planes while they are out of focus, it is possible to learn what may be a very useful modification of the artificial optical instrument called the camera obscura. If we cannot discard the superposed images out of focus, and see only among them the one in focus, it happens fortunately that the image in focus is stronger, better defined, and consequently more conspicuous than all the others. If we cannot discard entirely the images out of focus, they at all events appear only like a number of blended shades of the principal image. Therefore in this process for changing the power and the focus of the double combination of lenses according to the distance of the various planes, we do nothing but imitate one of the most beautiful and indispensable of natural contrivances, by which the eye is so wonderfully well calculated to perform all the exigencies of perfect vision, and is one of the most marvellous and splendid works of the Creator.

This new plan of operating not requiring a longer sitting than the old process, the interposition of the usual diaphragm will, by cutting off the oblique rays, increase the definition of the compound image. It follows that, as much as the intensity of light will allow, the smaller the aperture of the diaphragm is, the more perfect will be the result.

One of the great advantages of the method I have described is that the various planes of the figure are represented with the same intensity of light, which is not the case when the rays are more condensed on the plane of exact focus than on the other planes. For it is obvious that the difference of intensities of light on the various planes produces an unnatural effect, and destroys so far the harmony of the picture.

I have felt justified in bringing this matter before the Association, from the confident hope that, by the examination of scientific photographers, a new era may henceforth begin in the art of photography. If the plan I propose is in its present state deficient in many practical points, as must be the case in almost all new inventions, I am sure that, with the cooperation of so many ingenious and active minds which are constantly engaged in the task of progress, the science of optics will be able to supply photographers with a camera obscura which in its working will approach as near as an artificial instrument can approach the beautiful instrument which gives to man the most perfect perception of all the wonders and beauties of nature.

XXVIII. *Notes on Mineralogy.* By the Rev. SAMUEL HAUGHTON, M.D., Fellow of Trinity College, Dublin\*.

[Continued from vol. xxiii. p. 52.]

No. XII. *Analysis of Sombrerite.*

THIS rock-mineral is found at Sombrero and other isles of the Antilles, and is imported into Liverpool as a mineral manure. It is formed from the atmospheric decomposition of Guano, and contains numerous casts of land shells.

*Sombrerite.*

	Per cent.
Silica . . . . .	0·08
Phosphate of lime and alumina .	89·64
Carbonate of lime . . . . .	5·00
Chloride of potassium . . . . .	2·81
Fluoride of calcium . . . . .	0·10
Water . . . . .	0·60
	<hr/> 98·23
Loss . . . . .	1·77
	<hr/> 100·00

No. XIII. *Analysis of Pitchy Iron Ore from Kilbride, Glenslinkeen, co. Wicklow.*

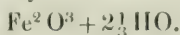
This ore is associated with Limonite and Psilomelane, and occurs in considerable quantity. It forms one of the large group of hydrated peroxides of iron, with a larger amount of water than is commonly found.

It contains no sulphur, no protoxide of iron, and no organic matter.

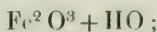
*Pitchy Iron Ore, Kilbride.*

	Per cent.
Peroxide of iron . . . . .	77·15
Water . . . . .	20·43
Silica . . . . .	0·30
Alumina . . . . .	trace
Phosphoric acid . . . . .	1·60
	<hr/> 99·48

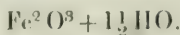
The result of this analysis is



That of Göthite is



and of Limonite



\* Communicated by the Author.



No. XIV. *Analysis of Green Orthoclase from Greenland.*

	Per cent.	Atomic constitution.		
Silica . . . .	64.40	1.431	1.431	4
Alumina . . . .	18.96	0.364	} 0.377	1
Peroxide of iron . . . .	1.04	0.013		
Lime . . . .	0.45	0.016	} 0.377	1
Magnesia . . . .	0.14	0.007		
Soda . . . .	2.35	0.076		
Potash . . . .	13.07	0.278		
	100.41			

This orthoclase was brought to Dublin from Greenland by Sir Charles Giesecké, and is beautifully crystallized in flat tabular masses. It gives the usual formula,

No. XV. *Analyses of Volcanic Rocks from New Zealand.*

I am indebted to Dr. Lauder Lindsay for the opportunity of making the following analyses of volcanic rocks from Dunedin in New Zealand.

1. *Basalt*, with visible crystals of Augite and Chrysolith. Dunedin, New Zealand.

	Per cent.
Silica . . . . .	46.60
Alumina . . . . .	16.80
Peroxide of iron . . . .	7.28
Protoxide of iron . . . .	5.76
Protoxide of manganese . .	0.72
Lime . . . . .	9.65
Magnesia . . . . .	6.89
Soda . . . . .	6.78
Potash . . . . .	2.08
Titanic acid . . . . .	trace
	102.56

2. *Vesicular Augitic Lava*, with cavities destitute of lining crystals. Mount Eden, Auckland, New Zealand.

This lava is divisible into two portions, soluble and insoluble in muriatic acid:—

Soluble . . . . .	38.2
Insoluble . . . . .	61.8
	100.0

It contains only a small quantity of carbonates, and seems to have undergone but little metamorphic action.

	Insoluble. grs.	Soluble. grs.
Silica . . . . .	33·20	13·50
Titanic acid . . . . .	1·10	0·31
Alumina . . . . .	8·80	2·90
Peroxide of iron . . . . .	2·14	0·60
Protoxide of iron . . . . .	2·70	5·70
Protoxide of manganese . . . . .	0·16	0·10
Lime . . . . .	5·40	2·52
Magnesia . . . . .	2·76	8·55
Soda . . . . .	3·74	2·23
Potash . . . . .	0·54	0·23
	<hr/> 60·54	<hr/> 36·64
Loss . . . . .	1·26	1·56
Total . . . . .	<hr/> 61·80	<hr/> 38·20

3. *Vesicular Augitic Lava*, with cavities lined with white crust. Dunedin, New Zealand.

This lava, like the last, is divisible into two portions, soluble and insoluble in muriatic acid:—

	Per cent.
Soluble . . . . .	40·40
Insoluble . . . . .	59·60
	<hr/> 100·00

It contains a large quantity of carbonates, due to metamorphic action.

	Insoluble. grs.	Soluble. grs.
Silica . . . . .	33·00	9·24
Titanic acid . . . . .	0·80	0·30
Alumina . . . . .	9·00	4·44
Peroxide of iron . . . . .	2·09	4·07
Protoxide of iron . . . . .	1·15	4·43
Protoxide of manganese . . . . .	0·16	0·10
Lime . . . . .	8·08	2·13
Magnesia . . . . .	3·04	6·09
Soda . . . . .	1·76	0·83
Potash . . . . .	0·88	0·21
	<hr/> 59·96	<hr/> 31·84
Gain . . . . .	0·36	
	<hr/> 59·60	
Carbonic acid, water, and loss. . . . .		8·56
		<hr/> 40·40

The portion of a lava that is soluble in muriatic acid consists of carbonates, magnetic oxide, and an unknown silicate of alumina and soda; it therefore varies considerably according to the

degree of metamorphism the lava has undergone subsequent to its emission. On reducing the insoluble parts of the preceding lavas to percentages, we find—

*Insoluble portion of Dunedin Lava.*

	No. 1.	No. 2.
Silica . . . . .	53·72	55·37
Titanic acid . . . .	1·78	1·34
Alumina . . . . .	14·24	15·10
Peroxide of iron . . .	3·46	3·51
Protoxide of iron . .	4·37	1·93
Protoxide of manganese.	0·26	0·27
Lime . . . . .	8·74	13·56
Magnesia . . . . .	4·46	5·10
Soda . . . . .	6·05	3·00
Potash . . . . .	0·87	1·47
Loss or gain . . . .	+2·05	—0·65
	<hr/> 100·00	<hr/> 100·00

This seems to be a mixture of Labradorite and Augite, and is very constant in the two specimens examined.

No. XVI. *On the Chemical Composition of four Zeolites, presented by Colonel Montgomery to the Geological Museum of Trinity College, Dublin.*

Some months ago, Colonel Montgomery presented to the Geological Museum of Trinity College some fine specimens of Zeolites found by him in the Bombay Presidency, four of which seemed to me worthy of chemical analysis and of being recorded.

No. 1. *Apophyllite.*

This mineral occurs in fine clear crystals coating the foliated Stilbite No. 2.

These crystals occur in the dimetric system.

Its chemical analysis gave the following results:—

		Oxygen.	
Silica . . . . .	51·60	26·791	} 26·902
Alumina . . . . .	0·24	0·111	
Lime . . . . .	25·08	7·130	
Magnesia . . . . .	0·08	0·031	} 8·175
Soda . . . . .	0·63	0·160	
Potash . . . . .	5·04	0·854	
Water . . . . .	16·20	14·399	
Fluorine . . . . .	0·97		
	<hr/> 99·84	<hr/> 49·476	

This analysis agrees very well with those of Apophyllite given in the books, but it is very difficult to assign its rational formula. It has been proposed to borrow as much oxygen from

the water as, added to that of the protoxides, would give the formula



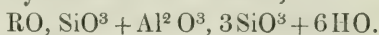
and such a substitution is mathematically possible in this example; I have no faith, however, in such imaginary combinations.

The Stilbite (No. 2) occurred in flat radiated crystals, readily distinguishable by the eye as those of Stilbite. Its analysis gave—

No. 2. *Stilbite*.

		Oxygen.
Silica . . .	58·20	30·217
Alumina . . .	15·60	7·291
Lime . . .	8·07	2·294
Magnesia . . .	none	
Soda . . .	0·49	0·125
Potash . . .	0·92	0·155
Water . . .	18·00	16·000
	<hr/> 101·28	<hr/> 56·082

This analysis gives very well the usual formula of Stilbite, regarded as an hydrated lime orthoclase,



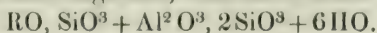
The foregoing analysis may be compared with that of very finely-crystallized Stilbite, found by Mr. Jacob in the Nerbudda Valley, which was published by me in Note V. on Mineralogy, in the Philosophical Magazine for July 1857.

The next mineral to be described is especially interesting, because it seems to set at rest the controversy as to the specific identity of Hypostilbite, and fully establishes the title of that mineral to be regarded as a distinct species, and not a degradation of Stilbite produced by hydrous metamorphism. It occurs in large, fibrous, transparent masses, radiated like Natrolite or Thomsonite, and filling globular cavities in green trap.

No. 3. *Hypostilbite*. Spec. grav. = 2·180.

		Oxygen.
Silica . . .	52·80	27·414
Alumina . . .	17·12	8·001
Lime . . .	7·89	2·242
Magnesia . . .	trace	
Soda . . .	2·35	0·601
Potash . . .	0·07	0·011
Water . . .	18·52	16·462
	<hr/> 98·75	<hr/> 54·731

This analysis is very like that published by me, of a specimen of Hypostilbite from Skye (Phil. Mag. July 1857), and also resembles the original analysis of Beudant. It may be regarded as an hydrated lime oligoclase, with the formula





The fourth specimen of Zcolite to be described occurs in large massive nodules, filling cavities in trap, of feathery structure, and apparently metamorphic in origin.

No. 4. *Harringtonite.* Spec. grav. = 2.174.

Silica . . .	45.60	Oxygen.	23.676
Alumina . . .	27.30		12.760
Lime . . .	12.12		3.444
Magnesia . . .	trace		
Soda . . .	2.76		0.707
Potash . . .	0.63		0.106
Water . . .	12.99		11.545
	101.40		52.238

This mineral is identical with the Harringtonite of the books; but it seems difficult to assign its true formula.

#### No. XVII. *On the Geometrical Forms of Gall-Stones.*

The gall-stones examined by me, whose geometrical figures are here noticed, were taken, after death, from six individuals; and I am indebted, for the opportunity of describing them, to Dr. Banks, Dr. Fleming, Dr. Foot, and Mr. Duffey.

The dihedral angles were measured by the goniometer, and may be classified as follows:—

#### No. I. *Angles nearly equal to 90°.*

1. . . .	90 0
2. . . .	90 15
3. . . .	90 0
4. . . .	90 0
5. . . .	94 30
6. . . .	90 0
7. . . .	90 0
8. . . .	90 0
9. . . .	91 0
10. . . .	90 0
11. . . .	89 15
12. . . .	88 0
13. . . .	86 0
14. . . .	89 30
15. . . .	92 0
16. . . .	94 0
17. . . .	94 0
18. . . .	90 0
Mean . .	90 28 $\frac{1}{4}$

#### No. II. *Angles nearly equal to 70° 31'.7.*

1. . . .	74 15
2. . . .	75 0
3. . . .	72 30
4. . . .	69 30
5. . . .	71 0
6. . . .	70 0
7. . . .	71 30
8. . . .	72 30
9. . . .	67 0
10. . . .	66 0
11. . . .	67 0
12. . . .	72 0
13. . . .	72 30
14. . . .	72 0
15. . . .	73 0
16. . . .	72 0
17. . . .	70 0
18. . . .	68 0
19. . . .	73 0
Mean . .	70 59

No. III.		No. IV.	
<i>Angles nearly equal to 109° 28' 3".</i>		<i>Angles nearly equal to 116° 26'.</i>	
1.	109° 0'	1.	117° 0'
2.	104 0	2.	122 30
3.	108 30	3.	118 0
4.	104 0	4.	117 30
5.	105 0	5.	118 0
6.	102 0	6.	123 0
7.	112 0	7.	122 0
Mean	106 21	Mean	119 42

The angles already described are those belonging to four of the geometrical solids inscribable in a sphere, viz.—

1. Hexahedron	90°	18 angles.
2. Tetrahedron	70 31·7	19 „
3. Octahedron	109 28·3	7 „
4. Dodecahedron	116 26	7 „
Total	51	„

The remaining angles observed cannot be reduced to any of the preceding, but may be classified empirically as follows:—

No. V. <i>Angles observed.</i>		No. VI. <i>Angles observed.</i>	
1.	60° 0'	1.	99° 0'
2.	59 30	2.	97 0
3.	52 0	3.	99 30
4.	59 30	4.	101 0
5.	60 0	5.	99 0
6.	64 0	6.	97 0
Mean	59 9	7.	101 0
		Mean	99 4

No. VII. *Angles observed.*

1.	82° 0'
2.	82 0
3.	80 0
4.	78 0
5.	77 0
6.	81 0
7.	79 0
8.	83 0
Mean	80 15

The total number of observations in Nos. V., VI., VII. are—

No. V.	. . .	59	9	6 angles.
No. VI.	. . .	99	4	7 „
No. VII.	. . .	80	15	8 „
				<u>21</u> „

The foregoing investigation warrants the belief that gall-stones owe their geometrical forms to mutual pressure in the gall-bladder and duct, and not to crystalline forces.

[To be continued.]

## XXIX. *Proceedings of Learned Societies.*

### ROYAL SOCIETY.

[Continued from p. 152.]

May 3, 1866.—Lieut.-General Sabine, President, in the Chair.

THE following communication was read :—

“The Calculus of Chemical Operations, being a Method for the Investigation, by means of Symbols, of the Laws of the Distribution of Weight in Chemical Change.—Part I. On the Construction of Chemical Symbols.” By Sir B. C. Brodie, Bart., F.R.S.

In chemical transformations the absolute weight of matter is unaltered, and every chemical change, as regards weight, is a change in its arrangement and distribution. Now this distribution of weight is subject to numerical laws; and the object of the present method is to facilitate the study of these laws, by the aid of symbolic processes. The data of the chemical calculus, as indeed of every other application of symbols to the investigation of natural phenomena, are supplied by observation and experiment; and its aim is simply to deduce from these data the various consequences which may be inferred from them. The province of such a method commences where that of experiment terminates.

This part comprises the consideration of the fundamental principles of symbolic expression in chemistry, and also the application of the method to the solution of perhaps the most important of all chemical problems, namely, the question of the true composition, as regards weight, of the units of chemical substances.

Section I. In the first section certain definitions are given of those weights, and relations of weight, of which the symbols are subsequently considered. It may be regarded as containing an analysis of the subject of chemical investigation. The definitions are, of “a chemical substance,” “a weight,” “a single weight,” “a group of

weights," "identical weights," "a compound weight," "a simple weight," and "an integral compound weight."

The unit of a chemical substance is defined as that weight of the substance which at 0° Centigrade and 760 millims. pressure, and in the condition of a perfect gas, occupies the volume of 1000 cubic centimetres. This volume is termed the unit of space.

Section II. The second section treats of symbolic expression in chemistry. A "chemical operation" is defined as an operation of which the result is a weight. These operations are symbolized by letters,  $x$ ,  $y$ , &c. An interpretation is assigned to the symbols  $+$  and  $-$  as the symbols of aggregation and segregation—that is, of the mental operations by which groups are formed. The symbol  $=$  is selected as the symbol of chemical identity; the symbol 0 as the symbol of the absence of a weight, this symbol being identical with  $x-x$ . The symbol  $(x+x)$  is the symbol of two weights collectively considered and as constituting a whole.

The symbols  $xy$  and  $\frac{x}{y}$  are selected as the symbols of compound weights; and it is proved that with this interpretation these symbols are subject to the commutative and distributive laws

$$xy=yx,$$

$$x(y+y_1)=xy+xy_1,$$

and also to the index law

$$x^p x^q = x^{p+q}.$$

Section III. treats of the properties and interpretation of the chemical symbol 1, which is selected as the symbol of the subject of chemical operations, namely, the unit of space. With this interpretation the chemical symbol 1 has the property of the numerical symbol 1 given in the equation  $x1=x$ .

Section IV. Chemical symbols are here shown to be subject to a special symbolic law, given in the equation

$$xy=x+y.$$

This property, by which chemical symbols are distinguished from the symbols employed in other symbolic methods, is termed the "logarithmic" property of these symbols. A consequence of this property is that  $0=1$ , and that any number of numerical symbols may be added to a chemical function without affecting its interpretation as regards weight.

Section V. relates to the special properties of the symbols of simple weights, which are termed prime factors, from their analogy to the prime factors of numbers. These symbols differ, however, from



these factors in that, like the numerical symbol 1, they are incapable of partition as well as of division, which is a consequence of the condition  $xy = x + y$ .

The symbol of the unit of a chemical substance, expressed as a function of the simple weights of which it consists, is identical with the symbol of a whole number expressed by means of its prime factors,  $a^n, b^m, c^p, \dots$ . A general method is given for discovering the prime factors of chemical symbols.

Section VI. is on the construction of chemical equations from experimental data.

Section VII. On the expression of chemical symbols by means of prime factors in the actual system of chemical equations. The object of this section is to prove that the units of weight of chemical substances are integral compound weights, and to discover the simplest expression for the symbols which is consistent with this assumption.

Such an expression cannot be effected unless some one symbol be determined from external considerations. The unit of hydrogen, therefore, is assumed to consist of one simple weight, its symbol being expressed by one prime factor,  $\alpha$ , which is termed the *modulus* of the symbolic system. This assertion is the expression of an hypothesis which may be proved or disproved by facts, and the consequences of which are here traced.

The symbols of the elements are considered in three groups:—  
1. The symbols of the elements of which the density in the gaseous condition can be experimentally determined, and which form with one another gaseous combinations. 2. The symbols of carbon, boron, and silicon. 3. The symbols of other elements, which are determined with a certain probability by the aid of the law of Dulong.

For the method of constructing these symbols, which depends upon the solution in whole numbers of certain simple indeterminate equations, we must refer to the memoir itself.

The following symbols (p. 230) may serve as an illustration of the general results.

Prime factors.	Absolute weight in grammes.	Relative weight.
$\alpha$	0.089	1
$\xi$	0.715	8
$\chi$	1.542	17.25
$\nu$	0.581	6.5
$\phi$	1.305	15
$\kappa$	0.526	6

Name of substance.	Symbol.	Absolute weight in grammes.	Relative weight.
Hydrogen ... ..	$\alpha$	0.089	1
Oxygen ... ..	$\xi^2$	1.430	16
Water ... ..	$\alpha\xi$	0.804	9
Chlorine ... ..	$\alpha\chi^2$	3.173	35.5
Hydrochloric acid ... ..	$\alpha\chi$	1.631	18.25
Oxide of chlorine ... ..	$\alpha\chi^2\xi$	3.888	43.5
Hypochlorous acid ... ..	$\alpha\chi\xi^3$	2.346	26.25
Teroxide of chlorine... ..	$\alpha\chi^2\xi$	5.319	59.5
Chlorous acid ... ..	$\alpha\chi\xi^2$	3.062	34.25
Chloric acid ... ..	$\alpha\chi\xi^3$	3.777	42.25
Nitrogen ... ..	$\alpha\nu^2$	1.251	14
Ammonia ... ..	$\alpha^2\nu$	0.760	8.5
Protoxide of nitrogen ... ..	$\alpha\nu^2\xi$	1.966	22
Nitrite of ammonium ... ..	$\alpha^3\nu^2\xi^2$	2.860	32
Chloride of ammonium ... ..	$\alpha^3\nu\chi$	2.391	26.75
Phosphorus ... ..	$\alpha^2\phi^4$	5.541	62
Phosphide of hydrogen ... ..	$\alpha^2\phi$	1.519	17
Pentachloride of phosphorus ... ..	$\alpha^3\phi\chi^5$	9.319	104.25
Tetrachloride of phosphorus ... ..	$\alpha^2\phi\chi^3$	6.145	68.75
Oxychloride of phosphorus ... ..	$\alpha^2\phi\chi^3\xi$	6.869	76.75
Carbon ... ..	$\kappa^y$	0.536+y	6+y
Acetylene ... ..	$\alpha\kappa^2$	1.161	13
Marsh-gas... ..	$\alpha^2\kappa$	0.704	8
Alcohol ... ..	$\alpha^3\kappa^2\xi$	2.056	23
Ether... ..	$\alpha^5\kappa^4\xi$	3.308	37
Acetic anhydride ... ..	$\alpha^3\kappa^4\xi^3$	4.559	51
Acetic acid ... ..	$\alpha^2\kappa^2\xi^2$	2.682	30
Trichloroacetic acid ... ..	$\alpha^2\chi^3\kappa^2\xi^2$	6.146	68.75
Hydrocyanic acid ... ..	$\alpha\nu\kappa$	1.207	13.5
Cyanogen ... ..	$\alpha\nu^2\kappa^2$	2.324	26

Section VIII. Certain apparent exceptions are considered, in which it is not found possible to express the symbols of chemical substances by means of an integral number of prime factors, consistently with the assumption of the modulus  $\alpha$ .

#### GEOLOGICAL SOCIETY.

[Continued from p. 155.]

June 20, 1866.—Warrington W. Smyth, Esq., M.A., F.R.S.,  
President, in the Chair.

The following communications were read:—

1. "On the Structure of the Red Crag." By S. V. Wood, Esq.,  
F.G.S.

The Rev. O. Fisher having lately published a paper in which he

endeavoured to show that the Chillesford beds were beneath the Fluvio-marine Crag, Mr. S. V. Wood in this paper first drew attention to certain facts which appeared to him to prove the contrary view, especially the relations of the deposits as exhibited in pits at Wangford and at Thorpe, near Aldborough. The author then drew attention to the character of the fossils of the Red Crag as affording evidence of one of the most rapid changes in fauna that Geology affords; and he showed that this deposit contains the evidence of a transition by stages, from the oldest—where the affinities of the fossils are to a great extent with those of the Coralline Crag, and to a greater extent with the existing fauna of the Mediterranean—to the newer stages, in which the shells are very few, and confined to types peculiarly northern.

2. “Note on supposed Remains of the Crag on the North Downs, near Folkestone.” By H. W. Bristow, Esq., F.R.S., F.G.S.

An examination of these sands at Paddlesworth had convinced the author of their similarity to certain ferruginous clayey sands with masses of ferruginous grit, which occur in the Hampshire Basin and belong to the Woolwich and Reading series; and he therefore concluded that if the Kentish beds can be proved to belong to any other member of the Tertiary series, it is only to be done by the evidence of the fossils.

3. “On the Warp of Mr. Trimmer, its age and probable connexion with the latest geological events and changes of climate.” By the Rev. O. Fisher, M.A., F.G.S.

The author commenced by referring to the opinion of the late Mr. Trimmer respecting the origin of soils, that they are composed of the débris of the underlying rocks, together with transported materials. He then showed that the adventitious matter usually occurs filling furrows in the subjacent rock, and appears to have been carried forward in a plastic state, and not water-drifted. The author named it “trail,” and explained that the variation of soils arises from its incorporation with the disintegrated matter. The furrows were considered to be indications of the last denudation of the surface, and it was suggested that they may have been formed by land-ice. The ice-sheet having finally disappeared, the formation of the warp with its basal pebbles was considered to be due to meteoric action. The warp was then stated to be older than the last depression of the land, and to underlie the *Scrobicularia*-clay, while the gravels beneath the submarine forests at the mouths of many valleys were also supposed to be trail.

In conclusion, Mr. Fisher discussed the theories of M. Adhémar and Mr. Croll, showing that the events as traced in the former part of the paper agree with their views, and that their determination of the date of the commencement of the alluvial period (the period of the retirement of the sea from our lower valleys) coincides remarkably with that assigned to it on totally different grounds by Mr. Prestwich, of from 8000 to 10,000 years.

4. "On Faults in the Drift-gravel at Hitchin, Herts." By J. W. Salter, Esq., F.G.S.

The author described some faults exhibited in a cutting of the Great Northern Railway, passing through the Chalk and Boulder-clay gravel, and remarked that whatever system of movements affected Tertiary rocks disturbed also the deeper-seated strata, and assigned this as a reason why the older rocks are more faulted and jointed than the newer.

5. "On some Flint Implements lately found in the Valley of the Little Ouse river, near Thetford." By J. W. Flower, Esq., F.G.S.

The sands and flint-gravel on the right bank of the river Ouse at Thetford form a terrace 8 to 10 yards above the river, and about 40 yards distant from it; at a spot called Red Hill a large number of flint implements have lately been obtained from this gravel, at from 12 to 15 feet below the surface, and within a foot or less of the chalk on which the gravel rests; and some were found in the same gravel filling pot-holes in the chalk.

The author pointed out the exact correspondence, as regards geological position and relations, between the Thetford gravels and the flint-implement-bearing beds of Amiens, Abbeville, Fisherton, Icklingham, Hoxne, &c. He further noticed the close resemblance which these implements and some others discovered in England bear to those of the valley of the Somme; and concluded by expressing his dissent from Mr. Prestwich's conclusions, and stating his own views on their mode of accumulation, remarking that, in his opinion, these implements were manufactured prior to the severance of this island from the continent.

6. "On some evidences of the Antiquity of Man in Ecuador." By J. S. Wilson, Esq.

The western slope of the Cordilleras was stated by the author to be occupied with projected volcanic matter distributed in terraces, the most recent of which is but slightly above high-water mark; the second rises in some places 10 feet above the former, and is well seen in the lower part of the Esmeraldas river and in the valleys of its lower tributaries; above this rise four other terraces, respectively 8, 15, 12, and 6 feet above one another.

The second terrace contains in many places remains of articles of human art, broken pottery, earthen figures, and fragments of gold ornaments. This pottery stratum is traceable along a line of 80 miles of coast, and, by partial observations, is determined to occur under corresponding conditions for a distance of 200 miles more.

A section at Chancama was also described; it is 24 miles from the coast, 180 feet above the sea, and 50 feet above the Esmeraldas river, and exhibits undisturbed sea-distributed gravel and sands, 6 feet 6 inches in thickness, containing fragments of pottery.

7. "On the relations of the Tertiary Formations of the West Indies." By R. J. L. Guppy, Esq., F.G.S.

In this paper the author first briefly noticed the present state of our knowledge of the different formations occurring in the Caribbean



area, which he named respectively Eocene, Lower Miocene, and Upper Miocene, these names having reference to their relative position rather than to their positive age. It was stated that Eocene strata were as yet known to occur only in Jamaica; and the author then described the Lower Miocene deposits of Trinidad, Anguilla, and Antigua, and the Upper Miocene of San Domingo, Jamaica, Trinidad, and Cumana, giving sections illustrating the nature and position of the beds, and lists of the fossils found therein. Mr. Guppy then discussed the age of the Caribbean Miocene deposits of the different islands, giving the evidence on which the above-mentioned classification is founded, and a sketch of the deposits in other islands not included in it. In conclusion the author discussed the relation of the West-Indian Miocene deposits to the Tertiary strata of other regions, especially with regard to the migration of species and the Atlantis hypothesis; and he inferred that the Miocene of the West Indies must be included in the same great period of time as that of Europe, and may therefore be considered, in a geological sense, synchronous, that it is highly improbable that the West-Indian Miocene forms reached the localities where they occur as fossils by way of the Isthmus of Panama, or by an easterly route from Europe or from the Indian sea, and that it is probable that during the early and middle Tertiaries such a connexion existed between the shores of the Atlantic as admitted of the migration of organized beings from one side to the other, although the continents may not have been absolutely joined.

8. "On the discovery of new Gold-deposits in the district of Esmeraldas, Ecuador." By Lieut.-Col. Neale, Her Majesty's Chargé d'Affaires in Ecuador.

The author stated that unworked and hitherto unknown gold-deposits had been discovered in the district of Esmeraldas, Ecuador, and that the President of the Republic, who had received specimens of the gold of a very pure quality, purposed sending a scientific commission to report on the probable yield of the gold-district. Further, he recorded a recent influx of immigrants from California and Nevada to the gold-mines of Barbacoas in New Granada.

9. "On bones of fossil Chelonians from the Ossiferous Caves and Fissures of Malta." By A. Leith Adams, M.B., F.G.S.

The remains of more than one species of River-Tortoise, agreeing in their characters with the Helodians and Potamians, were stated to occur in the Maltese caves and fissures associated with exuvæ of the fossil elephant, *Hippopotamus Pentlandi*, *Myoxus Melitensis*, and birds (the last chiefly aquatic, including *Cygnus Falconeri*), a lizard, and one or more frogs. The author considered that the nature and arrangement of the deposits and the conditions of their fossil fauna clearly show that they had for the most part been conveyed into the above situations by the agency of large bodies of water, which at one time overflowed the greater portion of the eastern half of the island.

10. "On the discovery of remains of *Halitherium* in the Miocene beds of Malta." By A. Leith Adams, M.B., F.G.S.

The four upper beds of the Miocene formation of the Maltese group, more especially the Sand-bed and Nodule-bands of the calcareous sandstone, have yielded several forms of Cetaceans, teeth of *Zeuglodon*, one or more species of Dugong allied to recent forms, and *Balæna*; to these the author has added a tooth, an ear-bone, and some caudal vertebrae of the *Halitherium*.

11. "On the affinities of *Chondrosteus*, Ag." By John Young, M.D., F.G.S.

The object of this communication was to show, from the characters of the skeleton, that *Chondrosteus* belongs not to the Chondrosteian division of the Ganoids, as stated by Agassiz, but to the Holostean division, since it possesses a well-ossified basioccipital; and the lateral walls of the cranium are composed of bones answering to the cartilage bones of ordinary Teleosteans.

12. "On new Carboniferous genera of Crossopterygian Ganoids." By John Young, M.D., F.G.S.

In this paper the following new genera were described:—*Rhizodopsis*, *Strepsodus*, *Dendroptychius*, and *Rhomboptychius*, all of which were provisionally named some years ago by Prof. Huxley. Their generic distinctness has been fully established by specimens recently discovered. The relation of *Rhomboptychius* to *Megalichthys*, and the position of *Holoptychius* and *Rhizodus* in this subdivision of the Ganoids, are discussed in the latter part of the communication.

13. "On supposed burrows of Worms in the Laurentian Rocks of Canada." By Dr. Dawson, F.G.S.

The author communicated the discovery of perforations, resembling burrows of worms, in a calcareous quartzite, or impure limestone, of Laurentian age, from Madoc, in Upper Canada, but belonging to a somewhat higher horizon than the Eozoon-serpentines of Grenville.

### XXX. Intelligence and Miscellaneous Articles.

#### OBSERVATION ON THE PASSAGE OF THE SPARK OF AN INDUCTION-COIL THROUGH FLAME. BY A. KUNDT.

IF the current of sparks of an induction-coil be passed through the luminous flame of gas or of a candle, no alteration is seen in the flame, excepting that in the path of the sparks the flame is intensely luminous, and, under certain circumstances, this brightly luminous path of sparks is traversed by dark cross bands. When the polar wires are suitably introduced, it appears constant and steady. Yet if the flame is viewed in a slowly rotating mirror, or in one which is moved to and fro in the hand, this apparent constancy is found really not to exist; for, looked at in the mirror, the image does not seem constantly broadened, but the part above the spark appears alternating, like the flame of a chemical harmonicon when looked at in a ro-

tating mirror. From the upper point of the flame to the spark, the image in the mirror appears to have serrate incisions, and at the lower point of each dark incision there is a passing spark. During this transition of an individual spark, the flame, therefore, is always extinguished above. The part below the spark is constant and steady.

The reason of this extinction of the upper part of the flame by the spark is due to the fact that the spark causes a very rapid combustion of the gases on its path, and then by the mechanical pressure which the spark thereby exercises on all sides, the access of gas from below is prevented for a moment.

The extinction of the upper flame at each spark which passes is also seen by another mode of investigation, in the following manner:—

While the sparks pass through the flame, and in such a manner that the latter is apparently quite steady, it is viewed through a rotating disk in which there are several narrow slits. Viewed *at right angles* to the direction of the passing spark, the flame above the spark seems formed of bright and dark layers; viewed *in the direction* of the spark, layers in the proper sense are not seen, but dark circles rather continuously rising on the flame. It is best for the latter observation if one electrode is in the flame, the other remaining outside, and this latter is looked at from the side.

It is not necessary here to explain minutely in what manner this production of bright and dark lines by the cooperation of the alternating flame and momentary observation is brought about. The phenomenon depends essentially on the same principle as that on which an emerging jet of water, when looked at through a rotating disk, seems formed of individual drops. It is clear that the number and motion of the dark and bright layers of the flame alter with the number of slits of the rotating disk, and with the velocity of rotation.—Poggendorff's *Annalen*, May 1866.

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ON THE DEPORTMENT OF SOLUTIONS OF GLAUBER'S SALT ON REDUCTION OF TEMPERATURE. BY DR. F. LINDIG OF SCHWERIN.

As the physical processes in the so-called supersaturation of Glauber's salt solutions have as yet found no sufficient explanation, either from physicists or chemists, it will not be uninteresting if I communicate a few observations on this subject.

If a solution of Glauber's salt, whether saturated or not, is allowed to cool slowly, it contracts with diminution of temperature, like any other body, as long as there is no crystallization. But as soon as the first crystals form in the clear solution, instead of contracting, it begins to expand, and continues to do so in proportion as the crystallization proceeds. Hence the density of the crystals forming is less than that of the solution from which they form\*.

Surprising as is this deportment of a gradually crystallizing solution of Glauber's salt, that of a so-called supersaturated solution is

\* With this the circumstance seems to disagree, that detached crystals did not swim in the liquid, but sank to the bottom.



still more surprising and remarkable. If such a one by careful treatment is cooled down to  $0^{\circ}$ , and then made to crystallize suddenly, the crystal cake formed, which constitutes a compact solid mass, exhibits an extraordinary increase in volume, and on further cooling, to about  $10^{\circ}$  C. below zero, contracts more and more. As in this condition of the original solution there can be no question of a separation of crystals as in the former case, it seems (like water below  $4^{\circ}$ ) not to follow the law according to which bodies contract by diminution of temperature.

The experiments in question, which any one can easily execute, I made with a glass flask of about 60 cubic centims. capacity, into which in different experiments I poured solutions of Glauber's salt of various strengths, covered them with a layer of petroleum, and closed the flask with a perforated caoutchouc stopper. Through this stopper passed a glass tube of 30 centims. in length and 2.09 cubic centims. in capacity, provided with a paper scale and reaching down to the layer of oil. To vary the temperature, the flask could be placed in a beaker containing either a freezing-mixture or warm water. If the crystallization of the enclosed solution did not take place spontaneously at the proper moment, it was immediately produced by a small particle of crystal projected through the open tube. The sudden change of temperature was frequently so energetic that the flask was cracked if the glass tube was accidentally stopped and presented no outlet for the displaced covering layer. The whole apparatus could be used as a thermometer (only in an inverse manner), and indicated a change of temperature of not too brief duration in a tolerably delicate manner. If, for instance; the strongly cooled apparatus was warmed with the hand for a few moments, a depression of the covering layer was distinctly perceived.—Poggen-dorff's *Annalen*, May 1866.

ON THE FIGURE OF THE EARTH. BY CAPTAIN. A. R. CLARKE.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

Ordnance Survey Office, Southampton,  
August 17, 1866.

The question of the correctness of the simple and direct application of the method of least squares to the determination of the figure of the earth, which is controverted by Archdeacon Pratt, is an important one, but, being purely mathematical, should not be a matter of opinion. As, however, it cannot be of great interest to the majority of your readers, I shall only ask leave to remark here that, so far from having vindicated the legitimacy of his "correction" of the method of least squares, his "improvement upon his correction" is not only expressly hypothetical and arbitrary, but is a still further departure from simplicity and truth. The values which Archdeacon Pratt, in his work 'On the Figure of the Earth,' had obtained for the local attraction at the "reference-station" of the three great arcs



were very nearly true; but by his improved method he has been led to entirely different and quite erroneous values.

I am, Gentlemen,

Your obedient Servant,

A. R. CLARKE.

ON THE ROTATORY ACTION WHICH QUARTZ EXERCISES ON THE  
PLANE OF POLARIZATION OF THE LEAST-REFRANGIBLE RAYS  
OF THE SPECTRUM. BY M. P. DESAINS.

In a memoir inserted in the *Annales de Chimie et de Physique*, 3<sup>e</sup> sér. vol. xxx., De la Provostaye and I investigated the rotatory action which *active* substances exert on the calorific rays of the visible spectrum. I have extended these researches to the obscure part of the solar radiation, and beg leave of the Academy to communicate the results which I have obtained.

At first, working with rays which, in the spectrum I used, occupied a position beyond the extreme red almost corresponding to the yellow, I observed that the plane of polarization of these rays only experienced a rotation of  $19^{\circ}$  when they traversed at right angles a plate of quartz capable of imparting a rotation of  $52^{\circ}$  to the mean red of the same spectrum.

This first fact obtained, I worked with rays still less refrangible, in the position on the side of the extreme red corresponding to the blue on the other side; I found heat-rays the plane of polarization of which only underwent a rotation of 8 or 9 degrees under the action of the quartz plate previously defined. Under equal conditions, the rotation of these rays was thus about one-sixteenth that of the extreme violet of M. Biot. Their wave-length would thus be four times that of the violet, if it be true that up to these extreme limits we could, as a just approximation, assume that these rotations are inversely proportional to the squares of the wave-lengths.

To observe conveniently the very feeble rotation whose value I have given, it is not necessary to work with rays isolated in the dark part of the spectrum. If a solar beam is sent through a pretty thick layer of solution of iodine in bisulphide of carbon prepared by Professor Tyndall's method, rays only are left which quite resemble those on which the observations above described have been made.

On this new point I have made a considerable number of experiments, of which I will describe one series.

A well-polarized solar ray, which had passed through a layer of iodized bisulphide, was quite extinguished when my analyzer indicated 45 degrees. The interposition of the quartz brought about an action on the rheometer; but this action again disappeared when the analyzer was brought to the division 55, and all observations made in other azimuths agreed in proving that the rotation was indeed 10 degrees. Here are the observations:—

Position of the analyzer.	Deflection.
55 .....	0
55 .....	0·1
— 35 .....	20·5
+ 10 .....	10
+ 100 .....	10·5

For positions of the analyzer equally distant from 55 the deflections are equal; and the sum of those obtained at +10 and +100 is equal to that obtained at —35, as it ought to be. The division of the scale employed in these measurements goes up to 180 on each side of zero. The quartz was always the same.

I shall finish this note by adducing some observations of a totally different nature, which appear to confirm my previous results. M. Dumoulin-Froment had the goodness to lend me a grating which he himself had constructed. On this delicate apparatus I let fall a solar pencil, transmitted through a narrow aperture, and concentrated by a lens; at a suitable distance I obtained, on a screen and with great distinctness, the phenomena of Fraunhofer. By placing the pile in the dark spaces which extend from one side to the other of the central pencil, I obtained no deflection. The needle, on the contrary, was sometimes deflected as far as 15 degrees by the action of the green, yellow, or red rays of the first spectrum. The limit of the extreme red of this spectrum touched the violet of the second. Receiving in addition the rays within this region, I obtained 10 degrees more of deviation; at a greater distance the effects rapidly decreased, and in the conditions of my experiments I only obtained a deflection of 2 to 3 when I received on the pile the orange and the yellow of the second spectrum, with the portions of red and of green the nearest these colours; but (and this is the point on which I dwell) by interposing in the path of the rays the trough full of iodized sulphuret, I extinguished all the effects produced by heat which are found in the visible part of the first spectrum, and as far as the violet of the second; while, when the pile was so placed as to receive the green, the yellow, and the orange of the second spectrum, the interposition of the sulphuret did not completely extinguish the calorific action. Such was then, in the *first* spectrum, the position of the obscure rays transmitted through the sulphuret. These latter results were obtained with a very delicate pile, constructed by M. Ruhmkorff according to the recent directions of M. Edm. Becquerel. —*Comptes Rendus*, June 11, 1866.

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ON THE USE OF NITROGLYCERINE IN THE QUARRIES OF VOSGESIAN SANDSTONE NEAR SAVERNE. BY M. E. KOPP.

The fulminating properties of nitroglycerine,  $C^6H^7(NO^1)^3O^6$ , and the experiments made with this substance in various localities of Sweden, Germany, and Switzerland, have led MM. Schmitt and Dietsch, proprietors of the great quarries of sandstone in the valley of the Zorn (Lower Rhine), to try its use also in their workings.

The success has been so great, both as regards economy and faci-

lity and rapidity of working, as to lead temporarily, at any rate, to the disuse of gunpowder, so that for the last six weeks quarries are worked with nitroglycerine only.

From the commencement we thought it necessary to prepare this substance on the spot; the carriage, whether by ship or by rail, of such a substance, so explosive and of such frightful power, appeared inadmissible. The great misfortunes which have occurred at Aspenwall and San Francisco have shown that these fears were well founded, and that the carriage of nitroglycerine ought to be absolutely forbidden.

After studying in my laboratory, with the aid of M. Keller, the various modes of preparing nitroglycerine (mixtures of glycerine with concentrated sulphuric acid and nitrates of potash and soda, or with nitric acids of different degrees of concentration), we have adopted the following method of manufacture, which has been established in a wooden cabin, constructed in one of the quarries:—

1. *Preparation of Nitroglycerine.*—In a vessel of sandstone placed in cold water, fuming nitric acid of 49° or 50° Beaumé is mixed with double its weight of the most concentrated sulphuric acid. (These acids are prepared expressly at Dieuze, and sent to Saverne.) On the other hand, glycerine of commerce, but free from lime and lead, is evaporated in an iron pot until it marks from 30° to 31° Beaumé. This concentrated glycerine should be syrupy when quite cold.

The workman places then 3300 grammes of the mixed acids, well cooled, in a glass flask (a sandstone pot, or a porcelain or sandstone basin may also be used), dipped in a bath of cold water, and pours slowly, with constant stirring, 500 grammes of glycerine. The important point is, to avoid a perceptible heating of the mixture, which would occasion a tumultuous oxidation of the glycerine with production of oxalic acid. Hence the vessel in which the change of glycerine into nitroglycerine is effected, should be constantly cooled on the outside by cold water.

The mixture having been completely effected, the whole is left for from five to ten minutes, then the mixture is thrown into cold water which has been previously agitated. The nitroglycerine is rapidly precipitated as a heavy oil, which is collected by decantation in a tall vessel; it is then washed once with a little water, which is decanted; then the nitroglycerine is placed in bottles, where it is ready for use.

In this condition the nitroglycerine is still a little acid and aqueous; but that is not inconvenient, for it is used a short time after its preparation, and these impurities by no means prevent its detonation.

2. *Properties of Nitroglycerine.*—Nitroglycerine constitutes a yellow or brownish oil, heavier than water (in which it is insoluble), soluble in alcohol, ether, &c.

Exposed to even a feeble degree of cold, provided it is prolonged, it crystallizes in elongated needles. A very violent shock is the best mode of exploding it. It is, moreover, managed easily, and without danger. Spread on the earth, it is only difficultly inflammable by a body in combustion, and only burns partially; a flask containing nitroglycerine can be smashed on the stones without the



liquid detonating; it may be volatilized without decomposition by a regulated heat; but if the ebullition becomes brisk, explosion ensues.

A drop of nitroglycerine falling on a moderately hot plate volatilizes quietly; if the plate is red-hot the drop inflames immediately, and burns like a grain of powder without noise; but if the plate, without being red, is hot enough to make the nitroglycerine boil immediately, the drop decomposes suddenly with a violent explosion.

Nitroglycerine, especially when it is impure and acid, may decompose spontaneously at the expiration of a certain time, with disengagement of gas, and production of oxalic and glyceric acids.

It is probable that to some such cause are due the spontaneous explosions of nitroglycerine of which we read in the papers. The nitroglycerine being enclosed in well-stoppered bottles, the gaseous products of decomposition, not being able to escape, exert a very great pressure on the nitroglycerine; and under these circumstances the least shock and the slightest motion may bring about an explosion.

Nitroglycerine has a taste at once saccharine, piquant, and aromatic; it is a poisonous substance; in very small doses it provokes strong headaches. Its vapour produces similar effects; and this circumstance might be an objection to its use in the deep galleries of mines, where the vapour cannot escape as easily as in the open air.

3. *Mode of using Nitroglycerine.*—Suppose it is desired to detach a layer of rocks. At a distance of from 2·5 to 3 metres from the outside, a mine-hole is dug of about 5 to 6 centimetres diameter, and 2 to 3 metres depth.

After having cleaned this of dirt, water, and sand, 1500 to 2000 grammes of nitroglycerine are introduced by means of a funnel.

A small cylinder of wood, of cardboard, or sheet iron about 4 centims. in diameter, and 5 to 6 centims. in height, is then introduced filled with ordinary powder. This is fixed to a wick or ordinary mine fuse, which penetrates into it to a certain depth, to assure the inflammation of the powder. By means of the match on the fusee the cylinder is lowered; and by the feel the moment can easily be judged at which the cylinder reaches the surface of the glycerine. The match being then held firmly, fine sand is run into the hole until it is quite full. It is useless to compress or tamp the sand. The match is cut a few centimetres above the orifice, and set fire to. In eight or ten minutes, the burning of the wick having reached the cylinder, the powder inflames. A violent shock ensues, which instantaneously explodes the nitroglycerine. The explosion is so sudden that the sand has no time to be projected.

The mass of the rock is seen to rise, become displaced, and settle down quietly without any projection; a dull sound is heard.

It is only on reaching the places that an idea is formed of the great force developed. Formidable masses of rock are displaced and fissured in all directions, ready to be worked mechanically.

The principal advantage consists in the fact that the stone is but slightly bruised, and that there is little waste. With the charges mentioned, 40 to 80 cubic metres of very resisting rock can be detached.—*Comptes Rendus*, July 23, 1866.



THE  
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AND  
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[FOURTH SERIES.]

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OCTOBER 1866.

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XXXI. *On the Absorption of Radiant Heat by Dry and by Moist Air.* By H. WILD\*.

THE results of the beautiful researches made, almost simultaneously, by Professor Magnus of Berlin and Professor Tyndall of London†, on the absorption of radiant heat by different gases, agree on the whole as closely as could be expected, considering the delicacy of the measurements. Hence it is the more striking that these investigators differ so widely in their statements concerning the absorption by dry and by moist atmospheric air.

Whilst Professor Magnus maintains, in the most recent publication known to me, that the moisture which, under ordinary circumstances, is mixed with air has only a very trifling, if any, influence on the absorptive power of the latter, Professor Tyndall infers from his old, as well as from his recent experiments, that the absorption is sensibly increased when dry air is mixed with aqueous vapour.

The decision of this disputed point has manifestly a considerable interest for meteorology; hence, on occupying myself during the past winter with the new phenomena of radiant heat, and after arranging an apparatus by means of which it was possible to demonstrate satisfactorily, according to a slightly modified form of Tyndall's method, the most important facts connected with the absorptive power of gases (even in my lectures on experimental physics), I felt myself induced to enter more closely into an examination of the point in question. The following de-

\* Translated from a separate impression communicated by the Author, having been read to the Scientific Society, Berne, June 9, 1866.

† [For an account of the order of sequence of these investigations see *Phil. Mag.* for April 1862, p. 252.—Eds.]

scription of my experiments will show how far I have been successful in deciding this question.

It must first be remarked that the results which the two investigators have obtained, each by his own method, do not differ, on closer consideration, so much as at first they may appear to do. Professor Magnus concludes, for instance, from his experiments with dry air and with air saturated at  $16^{\circ}\text{C}$ . with aqueous vapour, that the aqueous vapour existing in the air at this temperature exercises no perceptible influence on the absorption\*. The stratum of air which was here interposed between the source of heat at  $100^{\circ}$  and the thermopile was 1 foot in thickness†. The deflections of the galvanometer-needle amounted respectively to  $12^{\circ}\cdot 5$  and  $12^{\circ}\cdot 6$ ; the difference therefore falls below the mean error of observation,  $0^{\circ}\cdot 2$ . On the other hand, Professor Tyndall concludes from his measurements‡ that a stratum of air 4 feet in length, and saturated with aqueous vapour, absorbs, in round numbers, 10 per cent. of the whole radiation; and moreover this number holds good for the experiments where the tube was not closed by plates of rock-salt. Of every 100 incident rays, 90 passed through; or, to express it more correctly, if we denote by 1 the heating effect of the incident rays, that of the emergent ones was 0·90. Let us assume, as usual, that equally thick strata absorb equally, which is certainly admissible in the case of feebly absorbing moist air; then, according to this, out of every 100 incident rays 97·5 would pass through a stratum of moist air only 1 foot in thickness; in other words, the heating effect of the emergent rays would be to that of the incident rays as 0·975 to 1. This decrease of the heating effect would, in the experiments of Professor Magnus, have corresponded to a diminution of the deflection amounting to  $0^{\circ}\cdot 4$ ; so that the difference between the statements of the two investigators reduces itself in reality to a magnitude which does not exceed double the error of observation in one of the investigations.

An actual contradiction, however, exists between the results which Professor Magnus obtained, on experimenting according to the method of Professor Tyndall§ with a tube 0·66 of a metre long and open at both ends, and the statements of Professor Tyndall himself.

The deflections of the galvanometer-needle, which Professor Magnus observed on alternately introducing dry and moist air,

\* Phil. Mag. August 1861, p. 106.

† I merely consider here the experiments made by Professor Magnus with the source of heat at  $100^{\circ}$ , and omit those made with the gas-lamp, since the latter do not admit of being compared with Professor Tyndall's experiments.

‡ Pogg. Ann. vol. cxviii. p. 575. [Phil. Mag. July 1863, p. 21.]

§ Phil. Mag. S. 4. vol. xxvi. p. 24.

were, in fact, exactly opposite to those which Professor Tyndall observed under like circumstances, so that they corresponded to a diminished absorption due to the moisture of the air. Professor Magnus therefore held to his previously expressed view, that no difference exists between the absorption by dry and by moist air; and he sought to explain the opposite effect by the fact, recently established by him with greater accuracy\*, that all substances are heated when air reaches them which is moister than that which surrounds them, and that they are cooled when impinged upon by air which contains less moisture than that in which they are immersed. Since the principal contradiction, therefore, lies in the experiments made according to Tyndall's method, it was this method that I first employed.

### 1. *Experiments by Professor Tyndall's Method.*

The apparatus (without rock-salt plates) which I employed in this part of the investigations differs but slightly from that of Professor Tyndall. It consists of a thermopile of fifty bismuth-antimony elements collected in a brass cylinder of 2 centims. in diameter, which is provided at both ends with conical reflectors 12 centims. in length and having an external opening 6·5 centims. in diameter. Placed on its feet, the thermopile can be moved vertically and turned around a horizontal and a vertical axes. Its soldered parts are, of course, covered over as evenly as possible with lampblack. The poles of this thermopile are connected by conducting wires, first with a gyrotrope, and afterwards with a Meyerstein's electro-galvanometer. This instrument differs from the one described in Poggendorff's *Annalen*, vol. cxiv. p. 132, inasmuch as Herr Meyerstein, at my wish, has fixed the two auxiliary magnets underneath the wooden plate which carries the multiplier (for which purpose the feet of the plate were considerably lengthened), and has suspended the magnet, with its mirror, by a silk thread 60 centims. in length, which at its upper end is fastened to a glass tube carried by a copper stirrup. Besides a multiplier consisting of many windings of a thin wire, the instrument is provided with a second one, which was employed in the following experiments, and which consists of only twice 150 windings of a wire 1·5 millim. in thickness. Finally, in order more easily to obtain sufficient inertia, Herr Meyerstein has fixed a holder for a second magnet to the mirror-frame above the multiplier. This was likewise used in these experiments, by which means the greater of the auxiliary magnets could be dispensed with. By the approach of the small auxiliary magnet, the moment of inertia was increased so far as to obtain, without damping, a time of oscillation of the system of magnets amounting to 25 seconds in one set of experiments, and to 50 seconds in

\* Poggendorff's *Annalen*, vol. cxxi. p. 174. [Phil. Mag. S. 4. vol. xxvii. p. 241.]

the other. By means of the thick copper frame upon which the wire of the multiplier is wound, the oscillations of the magnet were very quickly damped. Finally, the observations of the deflections of the magnet were made either directly by means of a telescope and superjacent millimetre-scale, placed at a distance of 3 metres from the mirror, or by exhibiting the deflections in a dark chamber objectively upon a translucent scale. This was done by allowing the light from a gas-lamp, surrounded by a tin cylinder in which a slit was made, to fall upon the mirror, and by collecting the reflected light by means of a lens of great focal distance, so as to produce an image of the slit upon the translucent scale. The scale and slit were 2·3 metres from the magnet-mirror.

On each side of the thermopile a Leslie cube was placed at a proper distance, its blackened side being turned thereto, and in each cube water was kept boiling by means of a gas-lamp placed underneath. The vapour generated in the two cubes was conducted through glass and caoutchouc tubes into large vessels of cold water. The direct influence of the gas-flames on the thermopile was prevented by the interposition of a tin screen. Between the thermopile and the two sources of heat the tubes for the reception of the absorbing gas were placed; and these tubes, except in a single instance, were quite symmetrically arranged on the two sides of the thermopile; so that from them no inequalities whatever in the action of the equally distant sources of heat upon the thermopile could arise.

#### *First Series of Experiments.*

On each side of the thermopile was placed a brass tube, bright inside and out, 60 centims. in length and 6 in width, the ends of which were provided with perforated thin brass disks 12 centims. in diameter and placed perpendicularly to the axis. These disks did not diminish the opening itself, but were merely intended, in place of special screens, to prevent a direct radiation from the cube outside the walls of the tube to the thermopile. The ends of the two tubes were 10 centims. distant from the Leslie cubes, as well as from the funnel-shaped openings of the thermopile. Each of the tubes likewise possessed two lateral apertures, 15 centims. from the ends, both of which were provided with side tubes in order to introduce and carry away the gases.

To this end, each of the lateral apertures nearest to the thermopile were connected, by means of caoutchouc tubing, with a Wöhler's drying-tube; one of the latter was filled with pumice-stone moistened with concentrated sulphuric acid, whilst the pumice-stone in the other was moistened with distilled water. These two Wöhler tubes were also connected by means of a fork-shaped



tube with a small compression-pump provided with bellows which could be worked by the foot, just as in a blowpipe-apparatus. The current of air which this pump yielded divided itself at the fork and entered both tubes; it became saturated in the one with aqueous vapour, and in the other deprived by the sulphuric acid of all its moisture; consequently moist air was conducted to one of the tubes placed between the thermopile and the source of heat, and dry air to the other. In order that these currents of air might traverse the tubes and not at once escape at their nearest open ends, the most distant lateral apertures were connected with each other by a forked caoutchouc tube, and put in communication with an ordinary air-pump. In order to show the effect to several persons at the same time, I chose the objective representation of the position of the magnet-mirror. As soon as the magnet-mirror had quite come to rest (which always followed very quickly after the water in the two cubes had commenced boiling) and the pumps had been set in action, a motion of the image of the slit took place on the scale, amounting to about five divisions of the latter, each division being equal to a centimetre. The image remained in this position as long as the pumps were allowed to work (sometimes, with very short interruptions, for a quarter of an hour), and it returned slowly to its original position when the currents of air ceased. On interchanging the caoutchouc tubes leading from the two Wöhler tubes to the apparatus, so that the moist and dry air changed sides relative to the thermopile, a deflection of the magnet-mirror took place in the opposite direction. Through the momentary introduction of a metal screen on one side between the tube and thermopile, it was easy to recognize that the motion of the image on the scale *always indicated that the absorption of rays of heat by moist air exceeded that by dry air*. On repeating these experiments more than twenty times in the presence of several persons, I always obtained the same result, with very slight differences in the magnitude of the deflections. Professors Valentin and Schwarzenbach, moreover, were obliging enough to examine the direction of the deflections of the magnet-mirror, and thus to corroborate the above statement. The correctness thereof was likewise proved by the circumstance that a motion of the image of the slit in the same direction, but far beyond the limits of the scale, occurred when coal-gas instead of moist air was introduced into one of the tubes. Again, on several occasions, before the commencement or at the end of the observations, the Leslie cubes were removed, and the action on the thermopile was observed when, without any source of heat being employed, the pumps were put in action. When this was done energetically, a motion of the image, amounting to about one division

of the scale, always occurred in the opposite direction to the former one; that is to say, this motion indicated that the side of the thermopile upon which moist air was driven through the tube was most heated. It is doubtless this phenomenon which Professor Magnus also observed, and which has already been so well explained by him; nevertheless it appears to me to be more than probable that, in his experiments conducted according to this method, some action of the above kind prevailed over the absorption and produced the result opposed to the statements of Tyndall. The above experiment, however, removes another objection which perhaps might be raised against Tyndall's method. It might be supposed, for instance, that in the tube containing sulphuric acid, a development of heat takes place in consequence of the chemical action which ensues when the moist air gives up its vapour to the acid, and that this heat serves to warm slightly the dry air which issues; that, further, on the other hand, the evaporation of the water in the other tube, through which a current of air is passing, is accelerated, and that in consequence thereof an appreciable cooling takes place of the moist air which issues therefrom. According to this view, the observed deflection of the galvanometer-magnet would merely be a consequence of the lower temperature of the moist, and the higher temperature of the dry air. The same deflections, however, ought also to occur when, after removing the sources of heat, the forcing of air through the tubes is continued; but this does not take place. Nevertheless, in order to clear up this point quite satisfactorily, the gases were conducted in some experiments through pretty long thin metal tubes, interposed between the apparatus and the Wöhler tubes, and immersed in one and the same water-bath; this disposition of the experiment caused no change, however, in the above-described results. Since, lastly, in all the experiments the apparatus described was placed quite freely on a table in the middle of the room, all disturbing reflections of air-currents proceeding from lateral screens, and so forth, are out of the question.

After these more qualitative experiments I proceeded to exact measurements.

### *Second Series of Experiments.*

The apparatus was, in the next place, arranged in precisely the same manner as before, with the exception that the air was introduced into the tubes by the lateral apertures furthest from the thermopile, and the nearest apertures were connected with the air-pump. By this modification the disturbing action of air-currents upon the ends of the thermopile was quite avoided, as the following will show. The observation of the position of

the magnet-mirror was now made with telescope and scale, and in such a manner that the position was always read off on the scale as soon as, by continued pumping, the magnet was brought approximately to rest. The position of the magnet previous to the forcing-in of air was not noted, but instead of this the deflection to the opposite side was observed, consequent upon the previously-described interchange of the caoutchouc tubes, whereby the nature of the air in each of the two experimental tubes was altered. In this manner the following numbers were obtained :—

Left tube.	Right tube.	Scale-reading.	Difference.
		millims.	millims.
Moist air.....	Dry air .....	520	
Dry air .....	Moist air.....	410	110
Moist air.....	Dry air .....	440	
Dry air .....	Moist air.....	330	110
Moist air ...	Dry air .....	490	
Dry air .....	Moist air.....	370	120
Moist air.....	Dry air .....	440	
Dry air .....	Moist air.....	340	100
Coal-gas .....	Air in room ...	beyond 1000	
Air in room...	Coal-gas .....	beyond 0	

Decimetres rather than millimetres were noted here, since the magnet never came quite to rest. A heating of the right side of the thermopile produced a deflection towards the higher divisions of the scale. Lastly, the temperature of the room, and therefore also that of the air saturated with aqueous vapour, was 18° C. Assuming that the air on entering the tubes spreads solely to the side where the suction by the air-pump takes place, and that it there immediately leaves the tube, the interposed strata of moist and of dry air in the tubes would each be only 30 centims. thick; from the foregoing experiments, therefore, it would follow that by replacing a stratum of dry air 30 centims., or 1 foot thick, on one side of the thermopile by air saturated with aqueous vapour at 18° C., the thermal action of the source of heat at 100° on the corresponding end of the thermopile would be so far diminished as to cause a deflection of the magnet of our galvanometer amounting to 55 millims. of the scale, or, bearing in mind the stated distance of the scale from the mirror, to about  $\frac{1}{2}^{\circ}$ .

In order to be able to compare this absorption by aqueous vapour with that by coal-gas, for which purpose the above-mentioned experiments with coal-gas could not serve, the position of the magnet-system was so changed, by means of the auxiliary magnets, that the zero of the scale nearly appeared in the telescope when both tubes were filled with the air of the room.



When coal-gas was now introduced on the left-hand side and the air-pump allowed to work there only, a deflection of about 800 millims. occurred, which corresponds to a deflection of  $8^{\circ}$ . The substitution of ordinary coal-gas, therefore, on one side of the thermopile in place of a stratum 1 foot in thickness of the air of the room, caused a deflection of the magnet amounting to  $8^{\circ}$ , and corresponding to a diminution of thermal action. According to our experiments, therefore, the absorbing effect of a stratum of moist air 1 foot in thickness, and saturated with aqueous vapour at  $18^{\circ}$ , is only sixteen times smaller than that of coal-gas. It is self-evident that this number is only a rough approximation, since in such tubes, open at both ends, we cannot speak of a perfectly definite length of an interposed stratum of gas. According to the statements of Professor Tyndall, a stratum of coal-gas 4 feet in thickness absorbs 81 per cent., and one 1 foot in thickness absorbs 61 per cent. of the total radiation. Taking into account, therefore, the above given absorptions by moist air under similar circumstances, the absorption by coal-gas is, according to him, only eight times as great as that by moist air when the stratum is 4 feet thick, and twenty-four times as great when the thickness is only 1 foot. According to our experiments, therefore, the absorption by aqueous vapour is relatively somewhat greater even than Professor Tyndall has estimated it to be.

Moreover, with the above disposition of the apparatus no deflection whatever of the magnet-mirror could be observed when the two Leslie cubes were removed and the pumps again allowed to play. In fact the effect of the currents of air on the thermopile was rendered inappreciable by allowing these currents to enter at the most distant ends of the tubes.

With a second similar experiment we obtained 98 millims. as a mean of the difference of the readings of the scale, instead of 110. The temperature of the air at the time was  $16^{\circ}\text{C.}$ , and in order to dry and to moisten it, two sets of four U-shaped tubes were employed; the tubes of each set were connected by means of caoutchouc tubes and filled with pieces of glass, pure concentrated sulphuric acid being poured into the four tubes of the one set, and distilled water into those of the other.

In one of the following experiments, the above-described disposition of the apparatus was so modified as to obtain a single tube, 120 centims. long, on the left side of the thermopile, by placing both tubes end to end; in this manner the lateral apertures near the ends of the compound tube were at a distance of 90 centims. from one another. The lateral apertures near the middle of the long tube were connected with each other by a short caoutchouc tube. Finally, in order to produce perfect neutralization a double screen of metal was more or less interposed between



the thermopile and the source of heat on the right-hand side of it. This arrangement, therefore, corresponds exactly to that of Professor Tyndall. As to the rest, the procedure was again the same as before; that is to say, at the further end of the tube dry or moist air was introduced, and the end nearest to the thermopile was connected with the air-pump. The readings of the scale were as follows:—

Temperature.	Air in the tube.	Scale-reading.	Difference.
		millims.	millims.
18	Dry .....	340	230
	Moist .....	570	240
	Dry .....	330	240
	Moist .....	570	
	Moist .....	470	190
17	Dry .....	280	180
	Moist .....	460	

Here also a deflection towards increasing numbers was caused by heating the right-hand side of the thermopile; so that the increase of the deflection by 230 millims., when on the left 3 feet of dry air were replaced by air saturated with vapour at 18°, likewise indicated a simultaneous increase of the absorption of rays of heat.

Against all these experiments the objection might still be raised that, different kinds of gas-strata having been interposed on the two sides of the thermopile between the latter and the sources of heat, a different quantity of heat might have been reflected by them at their respective limits. In order to remove any such influence, which would certainly be a disturbing one, the following modified form of the apparatus was finally constructed.

### *Third Series of Experiments.*

In the new disposition of the apparatus, two new tubes, each 15 centims. long, but in other respects constructed similarly to the tubes 60 centims. in length already described, were introduced on opposite sides of the thermopile, and in such a manner that on the left, at a distance of 10 centims. from the funnel-shaped opening, the longer tube was placed; and then at 10 centims. beyond it came the shorter tube; and lastly, at a distance of 10 centims. from the last, the Leslie cube was placed. To the right, on the contrary, came first the smaller and then the greater tube, the intermediate distances being the same. Each of the short tubes was also provided with a lateral aperture. The three lateral apertures of the two tubes nearest to the thermopile, that is to say, of the long one on the left and the short one on the

right, were put, by means of fork-shaped caoutchouc tubes, in communication with one and the same caoutchouc tube, and the two most distant tubes were similarly connected with another caoutchouc tube. In this manner the same kind of air could be introduced on both sides into tubes of different lengths. The current of air was now furnished by a larger pair of bellows filled with air and pressed by weights; and in order to dry this air or to saturate it with aqueous vapour, four U-shaped tubes were employed, containing either concentrated sulphuric acid or distilled water.

A preliminary experiment was made by conducting alternately dry and moist air only into the two most distant tubes on opposite sides, so that each time on the right the stratum of air experimented upon was 45 centims. thicker than on the other side. For the sake of comparison, the tubes were lastly filled with coal-gas. The observations with telescope and a scale gave the following positions of equilibrium of the magnet-mirror:—

Gas in the outer tubes.	Scale-reading.	Difference.
	millims.	millims.
Dry air .....	390	18
Moist air .....	405	
Dry air .....	385	15
Moist air .....	395	15
Dry air .....	375	
Air in room .....	352	138
Coal-gas .....	490	

The differences are formed by comparing the mean of two readings for dry air, with the intermediate reading for moist air. The temperature of the air was 20° C. Now, since by heating the right-hand side of the thermopile (where the thicker gas-stratum was interposed) a deflection towards the smaller numbers of the scale ensued, these experiments also establish the greater absorption by moist air.

In order to increase the action, and in all cases constantly to maintain on both sides a current of the same kind of air towards the thermopile on the one hand, and the sources of heat on the other, dry air was conducted in a subsequent experiment into the outer tubes and moist air into the two inner ones, and these conditions were again reversed. In this manner the following results were obtained:—

Outer tubes.	Inner tubes.	Scale-reading.	Difference.
		millims.	millims.
Dry air .....	Moist air.....	550	
Moist air.....	Dry air .....	580	28
Dry air .....	Moist air.....	555	
Moist air.....	Dry air .....	590	30
Moist air.....	Dry air .....	606	
Dry air .....	Moist air.....	584	24
Moist air.....	Dry air .....	610	
Moist air.....	Dry air .....	512	
Dry air .....	Moist air.....	491	26
Moist air.....	Dry air .....	522	
Moist air.....	Dry air .....	517	
Dry air .....	Moist air.....	493	25
Moist air.....	Dry air .....	519	
Coal-gas .....	Dry air .....	738	
Dry air .....	Coal-gas .....	320	418

In these experiments the temperature was  $19^{\circ}$  C. It follows therefrom that moist air absorbs dark rays of heat more strongly than dry air; and by comparing the first differences with those given in the last experiment, where coal-gas and dry air were alternated with each other, it will at once be seen that the substitution of coal-gas in place of a stratum of dry air 45 centims. in thickness, causes an absorption about fifteen times as great as did the substitution of air saturated with aqueous vapour at  $19^{\circ}$  in place of an equally thick stratum of dry air.

This result, however, is only an approximate one; and notwithstanding its agreement with results previously obtained, it ought, strictly speaking, not to be compared therewith, because, as Professor Tyndall has shown, the absorption by coal-gas is not proportional to the thickness of the stratum passed through, but is much stronger in the first strata traversed than in the subsequent ones.

At all events, in these and in the former experiments no question can be raised as to whether a partial condensation of aqueous vapour or formation of dew may not have caused an increased absorption. It was the air proceeding from the bottom of the room which was always introduced into the apparatus; it must consequently have always had a lower temperature than the tubes standing above it, which, moreover, during the experiment were heated by radiation. Besides this, as already mentioned, unchanged results were obtained when the gases, before entering the tubes, were led through a water-bath whose temperature was lower than that of the air in the room.

It was by this last method that I exhibited objectively the difference between the absorption of heat by dry and by moist air, as well as by the ordinary air of a room, by coal-gas, and by the

vapour of ether, to the Scientific Society at their Meeting on the 10th of June. From the deflections of the galvanometer-needle the members were able to verify the fact of the greater absorptive power of moist air compared with that of dry air.

In conclusion, I may say that in all my experiments conducted according to Tyndall's method, which included more than a hundred distinct observations, I have *never* obtained deflections of the galvanometer-needle in contradiction to the statements of Professor Tyndall, that, further, my measurements give approximately the same ratio of the absorption by moist air to that by coal-gas, and that, lastly, I consider that certain objections which might have been raised against the conclusiveness of Professor Tyndall's experiments have been removed by means of appropriate changes in his method of experimenting.

This complete verification of Tyndall's results rendered it more desirable to investigate the absorption by dry and by moist air by the method of Professor Magnus.

## 2. *Experiments by Professor Magnus's Method.*

The characteristic features of Professor Magnus's method are that the thermopile is altogether within the tube destined to receive gases, and that this tube is closed at its ends by the sources of heat themselves. By this means we at once secure a contact between the gas and both sides of the thermopile, as well as between the gas and both the sources of heat; and, moreover, quite definitively defined strata of gas can be interposed between the sources of heat and the thermopile without using plates of rock-salt or other closing plates, which might disturb by their own absorption.

In order to combine the advantages of this method with those of Tyndall's, I had in the first place a tin tube prepared, about 4 feet long and 9 centims. wide; each of its ends was closed by one of the sides of a cube-shaped vessel of zinc, in which water was kept boiling by means of the introduction of vapour. At a distance of a foot from one end of the tube the above-described thermopile, deprived of its conical reflectors and its foot, lay freely in the horizontal axis of the tube, held by the pole wires. Between the pile and the nearest end of the tube were a diaphragm and a disk, of which the latter could be turned from the outside, in order, when requisite, to weaken the radiation of the nearest source of heat; on the side of the other source of heat were four similar diaphragms at about equal distances from one another. These diaphragms, as well as a vessel surrounding the tube up to near the sources of heat, and containing cold water, were intended to prevent heat being imparted to the thermopile by conduction or convection. In reality, however, this was so



ineffectually done that no (even approximately) constant position of the galvanometer-needle could be secured. Besides this, strong motions of the needle were caused whenever, by working the pumps, dry or moist air or coal-gas was allowed to enter or leave the tube through a lateral aperture.

In order to avoid currents of heated air, I arranged the apparatus for the following experiments more accurately, like that of Professor Magnus. In the first place the tube was placed vertically; the vessel in which water was boiled was placed at its upper end, and its lower portion was immersed in water contained in a large vessel of zinc. Within the tube and near the bottom the thermopile was again placed; and in so doing its lowest end was left free, whilst on its upper end the conical funnel of metal was replaced. This upper end was at a distance of 3 feet from the vessel in which water was boiled, and the radiation of the side walls was diminished by two interposed diaphragms. The lateral aperture for introducing and expelling the several gases lay between the boiling vessel and the uppermost diaphragm. The water in the zinc vessel, from which of course the pole wires of the thermopile were properly insulated, reached in the first experiments to a little above the lower diaphragm, and in the later experiments to the neighbourhood of the lateral aperture, and consequently to a little above the upper diaphragm.

The observations with this apparatus again showed, in the first place, strong deflections of the magnet-mirror of our galvanometer when air was leaving or entering the tube; and in fact in the former case these deflections indicated a cooling of the upper side of the thermopile, and in the latter an opposite effect. These deflections were much more intense than those produced by the total radiation of the upper source of heat of  $100^{\circ}$  upon the thermopile. These are the well-known thermal effects consequent upon compression and dilatation, and accordingly they manifested themselves when the boiling water was removed from the upper vessel. The influence of a compression or a dilatation of the air is always, in fact, first exerted on the upper side of the thermopile, since the latter is nearer to the place of entrance or exit\*. To these thermal actions is probably due, to some extent, the circumstance that I never, even when the water in the upper vessel had been maintained in a boiling state for three hours, could obtain a stationary condition of the temperature, and consequently an approximately constant position of the magnet-mirror. As a consequence of this, no well-marked difference

\* The thermal effects of the compression and dilatation were in our case so powerful and constant, that I found it most convenient, when showing the same in my lectures, to employ an apparatus constructed on this principle,

was apparent from the observations between the absorptions by dry and by moist air. And in fact such a difference could not have been detected, in consequence of the unsteadiness of the magnetic needle, since its effect would have corresponded at most to a few scale-divisions; for when I introduced coal-gas in place of dry air, the diminution of the deflection which the latter had produced did not amount to more than about forty scale-divisions. It was the more surprising to me, therefore, that even after waiting for a long time subsequent to the introduction of air or to its exhaustion down to a pressure of 16 mil-lims., the deflection caused by the radiation of the source of heat in the latter case was always from 100 to 200 scale-divisions or millimetres greater than in the former one. Now since the difference of the absorptions by very rare and by dense air can certainly not have caused this large difference between the deflections, we must conclude that in these experiments also conduction and convection had not been quite removed. It is true that, ordinarily, we assume that when heat is applied from above, as in the present apparatus, no currents of heated air can occur; to me, however, this assumption does not appear to be well founded. In the neighbourhood of the source of heat the surfaces of the tube, or at least the interior one, must gradually acquire a higher temperature by conduction, as well as by the effect of radiation, even when the tube is constantly cooled by contact with water; the heated sides of the tube must soon raise the temperature of the adjacent air, which thus becomes specifically lighter, rises, and gives place to other air; and this process must continue until the horizontal stratum of air under consideration has the same temperature as the sides of the tube. As soon as this occurs, however, the temperature of the sides of the tube at this height may again rise a little, or the same temperature may establish itself at a lower place, and thus, under the influence of the sides of the tube, the heat may gradually be propagated downwards from stratum to stratum, more through the mechanical motions of the heated air than through a proper conduction of the latter.

The insufficient sensitiveness on the one hand, and the above-described currents on the other, at length induced me to abandon the experiments by Magnus's method.

Although, therefore, this method of investigating absorption may, in the hands of so experienced and expert an experimenter as Professor Magnus, be an appropriate one for determining absolute values with great certainty, I feel bound, from my own experiences, to give a decided preference to Tyndall's method, not only on account of the greater facility with which it furnishes qualitative results, but also in consequence of its greater delicacy. It is principally in consequence of this greater delicacy

that, notwithstanding the negative results furnished by Magnus's method, I maintain that the greater absorptive power of moist air, as compared with dry, has been fully established by the experiments made according to Tyndall's method; and I am of opinion that meteorologists may without hesitation accept this new fact in their endeavours to explain phenomena which hitherto have remained more or less enigmatical. It appears to me to be desirable, however, to determine still more accurately the relative values of these two absorptions.

#### APPENDIX.

After the above had already been sent to press, I received the April Number of Poggendorff's *Annalen*, wherein Professor Magnus, in a paper "On the Influence of the Absorption of Heat on the Formation of Dew"\*, seeks to decide the above-disputed point relative to the absorption by dry and by moist air, by comparing experimentally the powers of emission of heated dry and moist air, and afterwards employing the principle of the equality of the ratio, in all bodies, between the powers of emission and absorption. From this comparison he found that air, saturated with aqueous vapour at the ordinary temperature of  $15^{\circ}$  C., emitted when heated to  $200^{\circ}$  only from two to three times as much heat as dry air, and that air passed through water (*durch Wasser gestrichen*) at a temperature of from  $60^{\circ}$  to  $80^{\circ}$  C. radiated only from six to seven times as much heat as dry air; he found, however, that dry carbonic acid and ordinary coal-gas radiated from thirty to forty times as energetically as dry air.

In my opinion, the disputed question is not only left undecided by these experiments, but is rendered thereby more complicated. In the first place, the results of these experiments are in contradiction to the statements of Professor Frankland, who on a former occasion stated that with a similar apparatus he had obtained a very strong radiation from heated aqueous vapour, as compared with that from dry air. Even if we assume, with Professor Magnus, that condensed vapour had here been produced, and that this had been the chief cause of the increased radiation of aqueous vapour, another peculiar divergence from the results of Professor Tyndall's and my own experiments still exists; for, on the one hand, it follows from the experiments of Tyndall that at ordinary temperatures air saturated with aqueous vapour absorbs heat from thirty to forty times as strongly as dry air does, whilst, according to Magnus, the latter radiates only from one-half to two-thirds as much as the former; on the other hand, however, Professor Tyndall's and my own measurements accord in giving a sixteen times as great

\* See Phil. Mag. for August 1866.



absorption to ordinary coal-gas as to moist air, and the same ratio of the radiating powers of these two gases is very nearly given by the above-mentioned results of the observations of Professor Magnus. In the last place, it must be observed that such experiments on radiation are not of themselves suited to decide definitively the present disputed point; for whilst the dry and the moist air, in the experiments of Professor Magnus on radiation, had a temperature of about  $200^{\circ}$ , the experiments on their absorption were instituted at the ordinary temperature of  $15^{\circ}$  C. The principle, however, according to which the ratio between the powers of absorption and radiation is the same for all bodies, is only true when the latter absorb and radiate at the same temperature. It is conceivable, therefore, that the absorption or radiation of the non-luminous rays by dry and by moist air may be very different at ordinary temperatures, although at a temperature of  $200^{\circ}$  they may be very nearly equal.

Berne, June 14, 1866.

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### XXXII. *On an Air-pump without Clearance.*

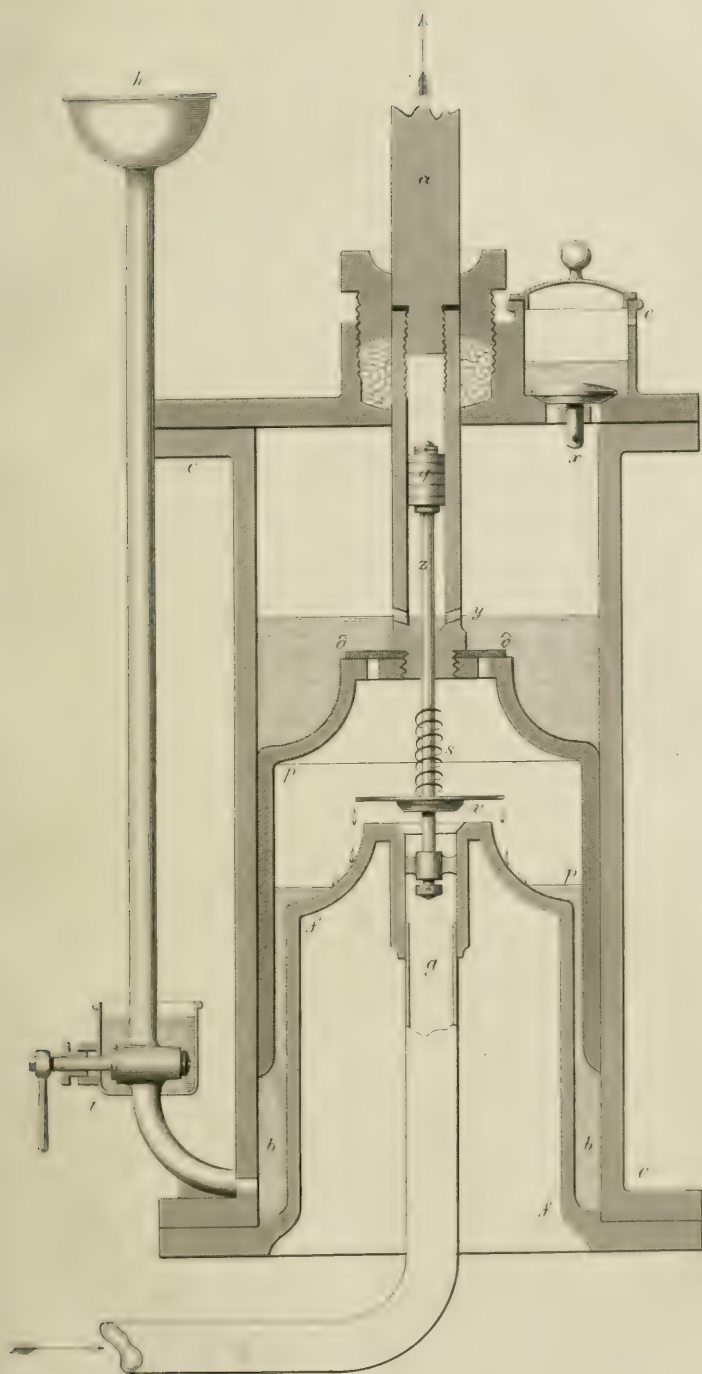
By ROBERT GILL\*.

[With a Plate.]

WITH air-pumps as ordinarily constructed, it is impossible to obtain a perfect vacuum, for two reasons. First, because the pump at each stroke can extract only a certain portion of the air contained in the receiver, and it follows evidently that another portion must always remain; but this consideration is not of practical importance, as, if we had a pump capable of extracting air from the receiver at each stroke without ceasing, we should soon reduce the pressure so much as to make it impossible for our instruments to indicate it. A second and more important reason is the following:—The air which the pump extracts from the receiver is of a tension lower than that of the atmosphere, and it loses more and more tension in proportion as the rarefaction becomes more perfect; this air enclosed in the pump-barrel must be discharged at each stroke either into the atmosphere or into a space in which the pressure is kept lower than that of the atmosphere: the valves which close the discharge orifices must have a certain weight, as, if they were in equilibrium, they would have no tendency to close the apertures; the rarefied air must be compressed so much as to acquire a pressure capable of raising the weight of the valves, in order to escape; and in ordinary air-pumps, not only must it overcome the weight

\* Communicated by the Author.







of the valves, but also that of the atmosphere which presses upon them. If the space in the pump-barrel could be diminished indefinitely, it is clear that the air contained in it would acquire a pressure equal to lifting any weight of valve, even if extremely rarefied at the beginning of the stroke. But this is far from being the case in our air-pumps; it is impossible that the piston should fit so perfectly the sides and the bottom of the cylinder as to fill *entirely* its capacity; and consequently a certain quantity of air must remain in the pump-barrel, which, expanding as the piston is raised, fills the pump and maintains in it a certain pressure which prevents other air entering from the receiver: the exhausting action must then necessarily cease.

To avoid this difficulty, Torricellian air-pumps have been contrived, in which a vacuum is obtained by filling a receiver with mercury and then allowing the mercury to run out through a vertical tube of such a height that the column of mercury contained in it overcomes the pressure of the atmosphere. It would be inconvenient to fill the principal receiver itself, so that an arrangement has to be made equivalent in action to the pump-barrel; this renders the apparatus complicated and difficult to manage. Besides, it is well known that, in order to expel the air completely from a receiver, it is not enough simply to fill it with mercury: as this liquid does not wet glass or metals with which it does not amalgamate (and these substances only can be practically used for the construction of such receivers), a stratum of air remains interposed between the liquid metal and the walls of the receiver, which of course prevents a perfect vacuum being formed when the mercury is run off; and this circumstance is demonstrated by the fact that barometer-tubes can be properly filled only by boiling the mercury in them. Moreover it has been proved that the Torricellian vacuum is not perfect, as it contains the vapour of mercury.

In order to remove these difficulties, the following apparatus has been contrived, in which clearance is totally avoided by filling the interstices between the cylinder and the piston with an inevaporable liquid, and in which all the joints are kept covered with liquid, so that no hiding-place is allowed to the air, which consequently must be expelled entirely at every stroke of the piston. Instead of the ordinary arrangement of two cylinders to balance the atmospheric pressure, I have preferred using only one, provided with a cover which prevents the atmosphere from pressing upon its piston. The bottom, *f* (Pl. IV.), of the cylinder is bell-shaped and ascends into the cylinder, leaving between its outer surface and the interior of the cylinder an annular space, *bb*; on the upper surface of this bottom is fitted the valve *v*, which alternately closes and opens the passage, *g*, to the receiver to be

exhausted ; to the valve *v* is attached the rod *sz*, which terminates in the leathern piston *q*, fitted to a cylindrical hole bored out in the piston-rod ; by means of this arrangement the valve *v* is opened by the ascent of the principal piston, and closed again when the piston descends. As will be seen further on, it is necessary that the valve *v* be kept closed until the piston have traversed a certain part of its upward stroke ; this is accomplished by means of the spring *s*, which, while compressed, overcomes the friction of the small piston and keeps the valve from opening ; but after the piston has ascended the given portion of the stroke, it remains expanded and ceases to act upon the valve, which therefore opens in obedience to the efforts of the piston *q*. The piston *pp* is similar in shape to the bottom of the cylinder, and its tubular portion works in the annular space left between the cylinder and its bell-shaped bottom ; into the upper part of the piston is screwed the rod *a*, which also serves to fix the inner edge of the leather ring *dd*, covering a series of apertures bored in the flat top of the piston. As mentioned above, the piston-rod is bored to receive the small piston *q* : as this last is required merely to open and close the lower valve, and as the compression of the air in the upper part of the hole would interfere with its proper action, there are channels cut upon its surface which allow the air to pass freely from one side of the piston to the other. The small piston-rod *z* is not fitted perfectly to the hole in the large piston-rod ; so that a narrow passage is left between the space under the piston and the small cylinder in the piston-rod, and by means of the apertures *y* a communication is made between the said small cylinder and the space above the principal piston : the effect of this arrangement is that a slight leakage is always maintained downwards through the piston. On the cover of the cylinder is fitted the self-acting valve *x*, of common construction, opening outwards, and surrounded by a vessel containing oil so as to ensure its perfect action.

To prepare the machine for work, the cover of the cylinder is removed, the piston is lowered to the bottom of its stroke, and then, opening the cock *i*, oil or other inévaporable liquid is poured through the funnel *h* into the cylinder, so as to cover the piston completely ; the cover being replaced and the cock shut, the apparatus is ready for action. On moving the piston upwards, the valve *v*, if free, would also move upwards and open ; but the spring *s*, being in a state of tension, keeps it upon its seat : and this is necessary, as, if the valve were free to rise, the apparatus being full of oil, some of it would enter the tube *g*, and might pass on to the receiver ; the valve is therefore kept closed by the spring. But as the piston is raised still higher, its tubular portion emerging further from the annular space *bb*, causes the



level of the oil under the piston to lower, and consequently the valve is left uncovered; the spring is so arranged that, as soon as this happens, it will have expanded so much as to be incapable of resisting the upward effort caused by the friction of the piston  $q$  against the principal piston-rod, and the valve  $v$  is therefore carried upwards and opened. The apparatus is now in the position shown in the figure: the space below the piston was completely full of oil, and the joints through which air might penetrate are all covered with this liquid; consequently the space left by the motion of the piston must remain perfectly empty, at least as regards air, as it is possible that even fixed oils might emit vapour of exceedingly low tension. The vacuous space below the piston being now in communication with the receiver through the tube  $g$ , becomes filled with air more or less rarefied; at the same time the air contained in the upper part of the cylinder being compressed by the ascent of the piston, raises the valve  $x$ , and escapes into the atmosphere through the aperture  $e$ . As the pressure above the piston is greater than that below it, a small leakage of oil takes place downwards through the interstice round the little piston-rod  $z$ , and dropping upon the shield attached to the valve  $v$ , falls into the annular space  $bb$ , and there accumulates during the ascent of the piston. The interstice for leakage allows only a small quantity of oil to pass; otherwise the valve  $v$  might be overflowed before the piston begins to descend, and consequently before the valve was closed. It will be seen that in every part of the piston's motion its lower edge is immersed in the oil, which prevents any lodgment of air between it and the sides of the cylinder—a circumstance which it is next to impossible to obtain in common air-pumps, as the piston cannot be in perfect contact with the cylinder; and it is evident that any such lodgment of air must prevent the total exhaustion of the receiver, as it will maintain in the cylinder a certain pressure, below which that in the receiver cannot fall.

At the commencement of the downward motion of the piston, the valve  $v$  is closed immediately by its piston  $q$ , and the valve  $x$  is closed by its own weight and the atmospheric pressure; the space below the piston becomes smaller and smaller as the piston descends; at the beginning of the upward stroke all the space below the piston was full of oil, and during the up-stroke more oil has passed down into the annular space; the consequence is, that when the piston reaches the bottom of its stroke, the space below being full, and in fact *more than full*, of oil, it is evident that the air extracted from the receiver must be completely expelled through the apertures  $dd$ , together with that small quantity of oil which passed downwards through the interstice around the rod  $z$  during the ascent of the piston. The

space below the piston is thus reduced absolutely *to nothing*, and consequently the air contained in that space is completely expelled, however rarefied it may have been on entering from the receiver; and it follows that the ascent of the piston will again leave a space perfectly empty, so that air will continue to flow into it from the receiver so long as it has a pressure sufficient to overcome its own inertia; and the action of the pump will continue perhaps for an indefinite number of strokes, so that the pressure in the receiver must soon fall so low as to become inappreciable to our most delicate instruments.

All the metallic parts of the pump should be made of iron, as brass or bronze would be rapidly corroded by the oil. As has been explained above, a slight leakage downwards takes place through the piston at each ascending stroke: this circumstance renders unnecessary that the piston should fit perfectly to the cylinder; so that a metallic fit without packing would be practically sufficient, as it is enough that the leakage during one stroke do not exceed the volume of the tubular portion of the piston. In order to be able to take the machine asunder, there should be a screw joint in the valve-rod *sz* close to the valve. When the cover is removed, the upper portion of the piston-rod *a* unscrewed, and the piston brought to the bottom of its stroke, the nut on the top of the piston *q* may be grasped by pincers and the rod turned so as to unscrew the joint above mentioned. The lower portion of the valve-rod is prevented from turning by the tail of the valve being square in section and fitted into a guide of similar shape. Once the small piston is removed, nothing hinders the removal of the principal piston and of the cylinder, and then the valve *v* remains free to be examined or cleaned. The joints above the piston do not properly form part of the pump, and the cover is adopted merely to prevent the atmosphere from pressing upon the piston; it is therefore unnecessary to have these joints covered with oil.

Palermo, September 1, 1866.

XXXIII. *Notes on Mineralogy*. By the Rev. SAMUEL HAUGHTON, M.D., *Fellow of Trinity College, Dublin*.

[Continued from p. 227.]

No. XVIII. *On the Meteoric Stone that fell at Dundrum in the co. Tipperary, on the 12th of August, 1865\**.

THE meteoric stone that forms the subject of the present paper, fell near Dundrum, co. Tipperary, under circumstances that were described to me as follows, by the man in whose garden it fell:—

\* Read before the Royal Irish Academy, 1866.

*Statement by eyewitness.*

"I, John Johnson, of the parish of Clonoulty near Cashel, co. Tipperary, was walking across my potato-garden at the back of my house, in company with Michael Fahy and William Furlong, on the 12th of August, 1865, at 7 P.M., when I heard a clap like the shot out of a cannon, very quick and not like thunder; this was followed by a buzzing noise which continued for about a quarter of an hour, when it came over our heads, and on looking up we saw an object falling down in a slanting direction; we were frightened at its speed, which was so great that we could scarcely notice it; but after it fell we proceeded to look for it, and found it at a distance of forty yards, half buried in the ground, where it had struck the top of a potato-drill. We were some time in looking for it (a longer time than that during which we had heard the noise). On taking up the stone, we found it warm (milk-warm), but not hot enough to be inconvenient. The next day it was given up to Lord Hawarden.—JOHN JOHNSON."

It was afterwards presented by Lord Hawarden to the Geological Museum of Trinity College, where it is publicly exhibited.

The stone weighed 4 lbs.  $14\frac{1}{2}$  ozs. It is rudely pyramidal in form, the triangular base being a freshly-broken surface, and the faces of the pyramid being covered by the usual black vitrified glaze. It is evidently a portion of a much larger stone; and as it appears from the foregoing statement that its vertical velocity was not great, it is probable that other pieces of the larger mass may yet be found in the neighbourhood of Dundrum.

A singular feature is observable in this stone that I have never yet seen in any other: the rounded edges of the pyramid are sharply marked by lines on the black crust, as perfect as if made by a ruler. This appearance is strictly confined to the surface, and seems to be a result of some peculiar tension of the fused crust in cooling; for no trace of any continuation of the lines can be found in the interior of the stone.

On examination with the lens, specks of metallic iron and of magnetic pyrites are visible, and also a few minute grains of chrysolite. No other minerals can be detected in the paste, which is of a dull grey, and of loose texture, almost like a porous sandstone; and the whole stone would attract little notice, were it not for its specific gravity and the metallic particles visible in it. The specific gravity of this meteoric stone, as is usually found to be the case, varied in specimens taken from different parts of the mass. The portion analyzed was found to have the following specific gravity:—

	grs.
Weight in air . . .	299·6
Weight in water . . .	201·9
Difference . . .	<u>97·7</u>

from which data the specific gravity is found to be

$$\frac{2996}{977} = 3.066.$$

Other portions of the stone gave a specific gravity of 3.57.

From 100 grs. acted on with iodine\*, which dissolved out the alloy of iron and nickel, there were obtained of peroxide of iron 27.95 grs., and of protoxide of nickel 1.20 gr.

The portion insoluble in iodine was now acted on with dilute muriatic acid, and gave the following results:—

	grs.
Silica . . . . .	12.92
Alumina . . . . .	0.15
Peroxide of iron† . . . .	9.87
Carbonate of lime. . . . .	0.50
Pyrophosphate of magnesia.	38.00
Potash and soda chlorides .	0.45
Platinochloride of potassium.	0.42
Oxide of manganese ( $Mn^3O^4$ )	0.05

On treating another 100 grs. of the stone for sulphur, with muriatic acid, and conducting the sulphuretted hydrogen into ammoniacal solution of sulphate of copper so as to form a black precipitate of sulphuret of copper, there were found, by the usual methods, 10.7 grs. of sulphate of barytes.

There were left, after the treatment with iodine and dilute muriatic acid, 42.1 grs. of mineral insoluble in these reagents.

From the solution by iodine, and the determination of sulphur as sulphate of barytes, we obtain—

	grs.	grs.
Peroxide of iron . .	27.95	19.57 iron.
Protoxide of nickel .	1.20	0.94 nickel.
Sulphate of barytes .	10.70	4.05 protosulphuret of iron.

Hence we obtain, as our primary analysis of the Dundrum meteoric stone,—

\* This method of investigation was suggested by Mr. William Early, assistant in the laboratory of Trinity College. The process consists in digesting the powdered mineral in iodine with water for twelve hours, and proved to be completely successful, as was shown by comparative trials on different portions of the powdered mineral.

† Present originally as protoxide and protosulphuret of iron.



1. *Primary Analysis of Meteorite (A).*

	Per cent.
1. Metallic iron . . . . .	19·57
2. Metallic nickel . . . . .	0·94
3. Magnetic pyrites . . . . .	4·05
4. Mineral soluble in dilute muriatic acid .	33·34
5. Mineral insoluble . . . . .	42·10
	<hr/> 100·00

The analysis of the earthy mineral soluble in dilute muriatic acid gives us (considering that 4·05 per cent. of FeS is equivalent to 3·68 per cent. of Fe<sup>2</sup>O<sup>3</sup>) the following result:—

2. *Soluble Mineral (A).*

	grs.	Per cent.	Oxygen.
1. Silica . . . . .	12·92	38·74	20·112
2. Alumina . . . . .	0·15	0·45	0·209
3. Protoxide of iron . . . . .	5·51	16·55	3·671
4. Protoxide of manganese .	0·05	0·15	0·033
5. Lime . . . . .	0·28	0·84	0·340
6. Magnesia . . . . .	13·65	40·93	16·358
7. Potash . . . . .	0·08	0·24	0·039
8. Soda . . . . .	0·17	0·51	0·130
9. Loss . . . . .	0·53	1·59	
	<hr/> 33·34	<hr/> 100·00	<hr/> 40·892

Adding together the oxygen of the protoxides, we find—

$$\begin{array}{rcl} \text{RO} & . & . & = 20·571 \\ \text{SiO}^3 & . & . & = 20·112 \\ \text{Al}^2\text{O}^3 & . & . & = 0·209 \end{array} \left. \vphantom{\begin{array}{rcl} \text{RO} \\ \text{SiO}^3 \\ \text{Al}^2\text{O}^3 \end{array}} \right\} = 20·321.$$

This result identifies the soluble mineral with Chrysolith (or olive), unless it be supposed to be a mixture of several minerals. Neglecting all the lesser constituents, we have—

$$\begin{array}{rcl} & \text{Oxygen.} & \\ \text{SiO}^3 & . & . & 20·112 \\ \text{FeO} & . & . & 3·671 \\ \text{MgO} & . & . & 16·358 \end{array} \left. \vphantom{\begin{array}{rcl} \text{SiO}^3 \\ \text{FeO} \\ \text{MgO} \end{array}} \right\} 20·029,$$

which gives very well the formula of Chrysolith,



The preceding analysis of the soluble portion of the meteorite was checked by the following proceeding. The 100 grs. from which the sulphur was determined having been acted on by the muriatic acid, the acid solution was evaporated to dryness and filtered, and the portion left on the filter was boiled with solution

of carbonate of soda, so as to redissolve the silica soluble in muriatic acid. There was left 42·44 grs. of insoluble mineral, while the soluble portion gave—

	grs.
Silica . . . . .	12·36
Peroxide of iron* . . .	38·60
Oxide of nickel . . . .	1·44
Carbonate of lime. . . .	0·40
Pyrophosphate of magnesia.	32·62
Potash and soda chlorides .	0·40

Assuming the iron (metallic) as 19·57 per cent., and the protosulphuret of iron as 4·05 per cent., we find—

	Per cent.
Equivalent of 19·57 Fe . .	27·94 Fe <sup>2</sup> O <sup>3</sup>
Equivalent of 4·05 FeS . .	3·68 „
	<hr/> 31·62

Subtracting this result from the total peroxide of iron, and converting the oxide of nickel into nickel, we obtain—

### 1. *Primary Analysis of Meteorite (B).*

	Per cent.
1. Metallic iron . . . .	19·57
2. Metallic nickel . . .	1·13
3. Magnetic pyrites . . .	4·05
4. Mineral (soluble) . . .	32·81
5. Mineral (insoluble) . .	42·44
	<hr/> 100·00

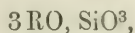
### 2. *Soluble Mineral (B).*

	grs.	Per cent.	Oxygen.	
1. Silica . . . . .	12·36	38·86	20·175	
2. Protoxide of iron . .	6·28	19·74	4·379	
3. Lime . . . . .	0·23	0·72	0·204	} 19·465
4. Magnesia . . . . .	11·72	36·85	14·727	
5. Potash. . . . .	0·07	0·22	0·036	
6. Soda . . . . .	0·15	0·47	0·119	
7. Loss . . . . .	1·00	3·14		
	<hr/> 31·81	<hr/> 100·00		

This result completely verifies that already found, and proves

\* Present originally as iron, protoxide of iron, and protosulphuret of iron.

the soluble mineral of the meteorite to be Chrysolith, having the formula



in which RO denotes protoxide of iron and magnesia.

The 42·10 grs. of mineral insoluble in muriatic acid were divided into equal parts, of which one was fluxed with carbonate of soda, and the other with lime and chloride of ammonium, with the following results:—

	grs.
Silica . . . . .	12·45
Alumina . . . . .	0·35
Peroxide of iron . . . . .	1·64
Oxide of manganese ( $\text{Mn}^3\text{O}^4$ ). . . . .	0·16
Peroxide of chrome ( $\text{Cr}^2\text{O}^3$ ) . . . . .	0·51
Carbonate of lime . . . . .	1·45
Pyrophosphate of magnesia . . . . .	12·45
Potash and soda chlorides . . . . .	0·80
Platinochloride of potassium . . . . .	0·90

Assuming the chromium to be present as chrome-iron, and making the necessary reductions in the other elements, we find—

	grs.
Original weight . . . . .	21·05
Chrome-iron . . . . .	0·75
Insoluble mineral . . . . .	20·30

### 3. Insoluble Mineral.

	grs.	Per cent.	Oxygen.	
Silica . . . . .	12·45	61·33	31·842	
Alumina . . . . .	0·35	1·72	0·803	
Protoxide of iron . . . . .	1·23	6·06	1·344	} 11·943
Protoxide of manganese. . . . .	0·16	0·78	0·174	
Lime . . . . .	0·81	3·99	1·133	
Magnesia . . . . .	4·47	22·02	8·800	
Soda . . . . .	0·28	1·38	0·352	
Potash . . . . .	0·17	0·83	0·140	
Loss . . . . .	0·38	1·89		
	20·30	100·00		

It is not possible to form any opinion as to the mineral composition of the insoluble portion of the meteorite, as it is doubtless composed of more than one unknown mineral substance.

If we collect into one view the preceding results, taking a mean of all, we obtain the following view of the mineralogical composition of the Dundrum meteorite:—

*Mineralogical Composition of the Dundrum Meteorite.*

	Per cent.	
1. Nickel-iron . . . . .	20·60	{ Iron 19·57 Nickel 1·03
2. Protosulphuret of iron . . . . .	4·05	
3. Chrome-iron . . . . .	1·50	
4. Mineral soluble in muriatic acid, probably Chrysolith . . . . .	33·08	
5. Minerals insoluble in muriatic acid.	40·77	
	<hr/> 100·00	

No. XIX. *On the Chemical and Mineralogical Composition of the Dhurmsalla Meteoric Stone\*.*

On the 14th of July, 1860, at 2.15 P.M., a remarkable meteoric stone fell at Dhurmsalla, in the Punjab; a small specimen of which was forwarded to the Geological Museum of Trinity College, which I have analyzed, with the results contained in the following paper.

The direction of the motion of the meteorite was ascertained to be from N.N.W. to S.S.E.

The cold of the fragments that fell was so intense as to benumb the hands of the coolies who picked them up and who were obliged, in consequence of their coldness, instantly to drop them.

The specific gravity of the Trinity College specimen was found as follows:—

	grs.
Weight in air . . . .	3335·4
Weight in water . . .	2354·1
Specific gravity . . .	= 3·399

The stone is grey, close-grained, and splintery in fracture, and presents fewer specks of metallic iron and magnetic pyrites than usual, and was coated with the ordinary black pellicle on its outer side.

From 100 grs. acted on with iodine, which dissolved the alloy of iron and nickel, there were obtained, of peroxide of iron 9·85 grs., and of protoxide of nickel 1·96 gr.

The portion insoluble in iodine was next acted on by dilute muriatic acid and evaporated to dryness at 212°, then moistened with muriatic acid and filtered, by which process it was divided into a soluble and insoluble portion; the portion left on the filter was boiled with carbonate of soda, so as to dissolve the free silica, which was found to be 18·95 grs. This was added to the portion originally soluble in muriatic acid, so as to give the following results:—

\* Read before the Royal Society, 1866.



	grs.
Silica . . . . .	18·95
Alumina . . . . .	0·14
Peroxide of iron* . . . .	14·11
Carbonate of lime . . . .	none
Pyrophosphate of magnesia .	51·31
Potash and soda chlorides .	0·30
Platinochloride of potassium	0·20
Oxide of manganese ( $Mn^3O^4$ )	0·66

On treating another 100 grs. of the meteorite for sulphur by boiling in muriatic acid, and conducting the sulphuretted hydrogen into an ammoniacal solution of sulphate of copper, so as to form a black precipitate of sulphuret of copper, there were found by the usual methods 14·8 grs. of sulphate of barytes.

There were left, after treatment with iodine, muriatic acid, and carbonate of soda, 38·3 grs. of the 100 grs. originally acted upon.

From the foregoing facts, we readily obtain, from the treatment with iodine and for sulphur—

	grs.	grs.	
Peroxide of iron . . . .	9·85	6·88	iron.
Protoxide of nickel . . .	1·96	1·54	nickel. [iron.
Sulphate of barytes . . .	14·80	5·61	protosulphuret of

Hence we find, as the primary analysis of the meteorite,—

### 1. *Primary Analysis.*

1. Metallic iron . . . . .	6·88
2. Metallic nickel . . . . .	1·54
3. Magnetic pyrites . . . . .	5·61
4. Earthy mineral (soluble) .	47·67
5. Earthy mineral (insoluble) .	38·30
	<hr/> 100·00

The results of the analysis of the soluble portion (considering that 5·61 of  $FeS$  is equivalent to 5·10 of  $Fe^2O^3$ ) give the following:—

### 2. *Earthy Mineral (soluble).*

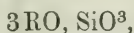
	grs.	Per cent.	Oxygen.
1. Silica . . . . .	18·95	39·75	20·637
2. Alumina . . . . .	0·14	0·29	0·135
3. Protoxide of iron . . . .	8·10	16·99	3·768
4. Protoxide of manganese .	0·66	1·38	0·308
5. Lime . . . . .	none		
6. Magnesia . . . . .	18·34	38·47	15·374
7. Potash . . . . .	0·04	0·10	0·016
8. Soda . . . . .	0·13	0·28	0·071
9. Loss . . . . .	1·31	2·74	
	<hr/> 47·67	<hr/> 100·00	<hr/> 40·309

\* Present originally as protoxide and protosulphuret of iron.

Adding together the oxygen of the protoxides, we find—

RO	. . .	19·537	
SiO <sup>3</sup>	. . .	20·637	} 20·772
Al <sup>2</sup> O <sup>3</sup>	. . .	0·135	

From the preceding result, it is evident that the soluble mineral in this meteorite is Chrysolith, or the silicate of magnesia and iron represented by the formula

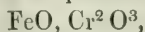


in which magnesia preponderates greatly over the iron.

The 38·3 grs. of mineral insoluble in muriatic acid and in carbonate of soda were now divided into two equal portions, of which one was fluxed with carbonates of soda and potash, and the other with lime and chloride of ammonium, with the following results :—

	grs.
Silica . . . . .	10·85
Alumina . . . . .	0·23
Peroxide of iron . . . . .	2·51
Oxide of manganese (Mn <sup>3</sup> O <sup>4</sup> ) . . . . .	0·30
Oxide of chrome (Cr <sup>2</sup> O <sup>3</sup> ) . . . . .	1·42
Carbonate of lime . . . . .	none
Pyrophosphate of magnesia . . . . .	11·50
Potash and soda chlorides . . . . .	0·30
Platinochloride of potassium . . . . .	0·50

Assuming the chrome to be present as chrome-iron,



we find

	grs.
Original weight . . . . .	19·15
Chrome-iron . . . . .	2·08
Earthy insoluble . . . . .	17·07

If we now omit the chrome-iron and make the necessary reductions in the foregoing results, we obtain—

### 3. *Earthy Mineral (insoluble).*

	grs.	Per cent.	Oxygen.
Silica . . . . .	10·85	63·56	33·000
Alumina . . . . .	0·23	1·34	0·525
Protoxide of iron . . . . .	1·60	9·37	2·078
Protoxide of manganese . . . . .	0·30	1·75	0·392
Lime . . . . .	none		
Magnesia . . . . .	4·13	24·19	9·666
Soda . . . . .	0·08	0·47	0·119
Potash . . . . .	0·09	0·52	0·087
[Gain] . . . . .	[0·21]	[1·20]	
	17·07	100·00	45·867

The oxygen of the protoxides of the preceding analysis amounts to 12·342 per cent.; but it would be fallacious to form any opinion as to the composition of the whole, so long as we are not acquainted with the constituent minerals that compose it.

Collecting together into one view the preceding results, we find—

4. *Mineralogical Composition of the Dhurmsalla Meteorite.*

1. Nickel-iron . . . . .	8·42	$\left\{ \begin{array}{l} \text{Iron} \quad . \quad 6·88 \\ \text{Nickel} \quad . \quad 1·54 \end{array} \right.$
2. Protosulphuret of iron . . .	5·61	
3. Chrome-iron* . . . . .	4·16	
4. Chrysolith (Peridot or olivine)	47·67	
5. Minerals insoluble in muriatic acid . . . . .	$\left. \begin{array}{l} \\ \end{array} \right\} 34·14$	
	100·00	

Trinity College, Dublin,  
June 1, 1866.

XXXIV. *On the Development of Hydrogen from the Anode.*

By Professor W. BETZ†.

**I**F a solution of an alkali or an alkaline earth be decomposed between magnesium electrodes, the negative wire undergoes no change either in appearance or weight, whilst the positive wire is dissolved with simultaneous evolution of hydrogen. The development of this gas under such circumstances was observed by Wöhler and Buff‡ in the case of another metal, aluminium; the process, however, was rendered more intricate by the presence of a considerable quantity of silicon, and the consequent formation of siliciuretted hydrogen. The greater simplicity of the action when magnesium is used recommends the employment of this metal for observations on this unusual electrolysis; for by its means we may not only trace the causes which act in this case, but likewise those influencing the phenomena observed when the terminals consist of aluminium wires.

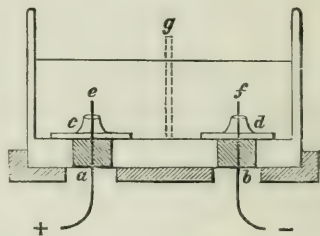
The magnesium wire made use of in the following experiments was from the works of Johnson, Matthey, and Co., of

\* The quantity of chrome found in this meteorite is unusually large, being represented by 2·84 per cent. of  $\text{Cr}^2\text{O}^3$ , and by 4·16 per cent. of  $\text{FeO}$ ,  $\text{Cr}^2\text{O}^3$ ; yet it is not without precedent, for in the meteoric stone that fell at Nobleborough, Maine, U.S.A., on the 7th of August, 1823, Webster found 4 per cent. of  $\text{Cr}^2\text{O}^3$ .

† Translated by Dr. W. Flight from Poggendorff's *Annalen der Physik und Chemie*, No. I, 1866.

‡ *Ann. der Chem. und Pharm.* vol. ciii. p. 218.

London. Unfortunately I could not procure wire of any other thickness than that of a moderate-sized knitting-needle, one metre weighing 0.44 grm. When exposed to the action of the current it was uncommonly quickly dissolved, so that I had to construct a special voltameter in order to maintain the action for a sufficient length of time. Two holes (*a* and *b*) were bored through the under surface of a glass vessel (see figure), and closed with tight-fitting corks. A round piece of caoutchouc was firmly cemented on each of these corks by means of gutta percha, and on each of these india-rubber plates was fastened a funnel-shaped cap (*c* and *d*). The wires (*e* and *f*) were passed through the corks and caoutchouc plates from below, so that the under surface of the vessel remained water-tight. Over the two funnels were eudiometers, held in their places by supports. A partition of porous ware (*g*) divides the vessel into two cells. The positive wire is quickly dissolved, and to replace it as fast as used, fresh wire is pushed up from below. Were it not surrounded by the cap (*c*) it would be immediately eaten through at the point projecting from the caoutchouc plate, where in fact the current is most powerful. The piece thus separated is carried away by the gas, and the experiment rendered useless for quantitative purposes. If an experiment is to be interrupted without leaving the wires exposed to the action of the electrolyte, they must be withdrawn, the edges of the holes in the caoutchouc plates closing the opening.



The gas from the anode never ignited spontaneously; in fact the magnesium contained so small a trace of silicium that the formation of siliciurettel hydrogen was not to be expected. Analysis of the gas showed it to consist of hydrogen alone. The accompanying phenomena at the positive wire, and the relative quantities of gas disengaged from the two poles, differed very greatly according to the nature of the electrolytes used; it was, however, in these accompanying circumstances that the cause of the anomalous development of hydrogen was found.

For most of my experiments I employed a solution of sulphate of magnesium, because I thought by the use of this liquid they would be least likely to be obscured by secondary action. The action was very similar to that which Wöhler and Buff observed in the case of aluminium in a solution of its chloride; that is to say, the positive wire was simply dissolved. I always noticed, however, that as soon as the wire was dipped in the



liquid it became black, and, moreover, that sometimes small particles of this coating were thrown off, rendering the solution in the eudiometer over the anode turbid. But in this case also the ratio of the quantities of hydrogen at the two poles was so nearly constant that this could scarcely be looked upon as an accidental coincidence. The subjoined Table contains the results of my determinations in seven series of experiments. The column headed Cu gives the weight in grammes of metal thrown down in a copper voltameter introduced into the circuit; H<sub>-</sub> and H<sub>+</sub> show the number of cubic centimetres of hydrogen reduced to 0° and 760 millims. pressure, respectively developed at the negative and positive poles. The columns superscribed Mg denote the quantities of magnesium equivalent, as the headings show, to the copper in the voltameter, to the hydrogen at the negative electrode, to the hydrogen at the positive electrode, and lastly to the sum of the two last mentioned, whilst the final column (Loss) gives the decrease in weight of the positive wire during electrolysis.

No.	Cu.	H <sub>-</sub> .		H <sub>+</sub> .		Mg.				
		Equiv. Cu.	Found.	Found.	$\frac{1}{3}$ H <sub>-</sub> .	Equiv. Cu.	Equiv. H <sub>-</sub> .	Equiv. H <sub>+</sub> .	Total.	Loss.
1	0.0780	27.3	27.12	9.36	9.04	0.0292	0.0290	0.0100	0.0390	0.039
2	0.0725	25.4	25.7	8.07	8.56	0.0272	0.0275	0.0086	0.0361	0.035
3	0.0780	27.3	26.9	11.06	8.97	0.0292	0.0288	0.0118	0.0406	0.041
4	0.1180	41.4	42.3	16.8	14.1	0.0442	0.0451	0.0180	0.0631	0.064
5	0.0800	28.7	29.4	13.2	9.8	0.0300	0.0314	0.0141	0.0455	0.045
6	0.0700	24.5	24.7	9.62	8.23	0.0262	0.0264	0.0103	0.0367	0.036
7	0.0730	25.6	24.8	9.8	8.26	0.0274	0.0265	0.0105	0.0370	0.039

It follows most unequivocally from this Table, that the loss in weight of magnesium is equivalent to the total hydrogen given off from both poles; the precipitated copper of the voltameter, on the other hand, is only equal to the hydrogen evolved from the cathode.

It is seen, moreover, by comparing the columns H<sub>+</sub> and  $\frac{1}{3}$ H<sub>-</sub>, that the quantity of hydrogen disengaged from the positive pole is somewhat more than one-third of that given off from the negative wire. In experiments 3 and 5 this excess is greatest; and as I was especially struck with the larger quantity of black incrustation thrown off in these two experiments, rendering the liquid in the eudiometer particularly cloudy, it occurred to me to seek, in the presence of this black body, the cause of the anomalous development of hydrogen. I endeavoured, therefore, to isolate it, and succeeded to a certain extent in doing so. If a solution of chloride of sodium be electrolyzed between two mag-

nesium electrodes (the negative plate can be replaced by a platinum electrode), a considerable quantity of black matter at once deposits on the positive pole. Part of this substance is swept off by the current of gas, part falls to the bottom. A gas is continually being developed from this substance, even when it is no longer in contact with the plate on which it was deposited. Collected in a eudiometer and analyzed, the gas proved to be hydrogen. If during the electrolysis the eudiometer be held firmly upon its caoutchouc plate so that none of the black matter can fall out, the current of course not being stopped, and if, lastly, the measuring of the gas-volumes, when the current has ceased, be delayed till there is no longer any gas disengaged from the precipitate, it is then found that the sum of the volumes of hydrogen evolved from the two poles is again equivalent to the magnesium dissolved; the ratio of the two gas-volumes, however, depends on the strength of the current.

In the two following experiments dilute solution of chloride of sodium was decomposed in the usual manner; in experiment 8 six Grove's cells were used, and in experiment 9 the magnesium wire which was to form the positive pole was directly fastened to the platinum wire as negative metal.

No.	H <sub>-</sub> .	H <sub>+</sub> .	$\frac{1}{3}$ H <sub>-</sub> .	Mg.			
				Equiv. H <sub>-</sub> .	Equiv. H <sub>+</sub> .	Total.	Loss.
8	14.9	10.0	4.96	0.016	0.011	0.027	0.027
9	3.78	10.8	1.26	0.004	0.0116	0.0156	0.017

The ratio of H<sub>-</sub> to H<sub>+</sub> was likewise never more than 3 to 1 when solution of chloride of ammonium was employed as electrolyte.

10 | 14.4 | 9.77 | 4.8 | 0.0151 | 0.0104 | 0.0258 | 0.026

In this case no black precipitate was formed.

If the black body produced by the electrolysis of a solution of chloride of sodium be allowed to remain in the liquid, it is soon covered with white flakes, and is finally converted into a white muddy substance. This consists of hydrate of magnesia. If the liquid be greatly diluted before this change is complete, the black body can be perfectly purified by stirring the solution briskly and pouring off the lighter white flakes. It undergoes but little change in water; by no method, however, have I succeeded in drying it unchanged: when under the receiver of the air-pump over sulphuric acid, as soon as it was nearly dry, it became grey, and a mixture of white and black particles could

then be clearly distinguished by a pocket-lens. Though I had on this account to abandon analyzing this body, its nature could be inferred from other circumstances. If the black precipitate, well washed, be placed in dilute acid, it dissolves with evolution of hydrogen. The solution contains no chlorine, so that it was not necessarily the electrolysis of a chloride which had caused the formation of this body; it is moreover identical with the incrustation formed in the solution of sulphate of magnesium. A substance which by decomposition of water and development of hydrogen oxidizes to magnesia, could only be magnesium, or a lower oxide of this metal, *suboxide of magnesium*. As the relation between the amount of the body dissolved and the volume of hydrogen generated could not be determined, this point could not be settled by analytical means. But, apart from the fact that no cause at all can be found why a separation of spongy magnesium should only take place at the positive pole, the precipitate in its electrical comportment resembled an oxide. If the current of a battery be passed through very dilute sulphuric acid between magnesium electrodes, the positive wire becomes immediately black. If the two wires be now connected with a galvanometer by means of the reverser, the positive wire is first positive and then becomes immediately powerfully negative, remaining so till the black incrustation has vanished. In an experiment the image of the scale of my reflecting galvanometer moved ten divisions to the positive side, but with the next swing of the mirror went over to the fiftieth division on the negative side, remained motionless there, and then went very slowly back to zero, whilst the wire became first covered with white spots and then entirely white. When I first observed this phenomenon I thought I had to do with an action similar to that already noticed in the case of iron\*, to which I gave the name of "anomalous polarization," but which Wiedemann† has called "positive polarization." I soon saw, however, that there were two different things to be distinguished here—a polarization, and the electromotive action of the black incrustation. The first deflection, the positive, is to be ascribed to a polarization. This quickly vanishes, and is caused by the development of hydrogen; for even in dilute acid hydrogen is evolved from the magnesium anode during electrolysis. That the negative plate appears not to be the most strongly positively polarized, but the positive plate covered with a negative layer of oxide, is not without precedent; for the negative body covered with hydrogen is often more positive than the positive itself: for instance, platinum in a gas-battery, when covered with hydrogen, is more positive than

\* Poggendorff's *Annalen*, vol. lxxiii. p. 415.

† *Lehre vom Galvanismus*, vol. i. p. 508.



copper\*. In any case, however, the second deflection shows that the black precipitate is negative towards magnesium; the negative nature vanishes with the black body itself. The entire proceeding is moreover independent of the closing of the secondary battery. If the battery-current be broken and connexion with the galvanometer be made only after the lapse of some time, the blackened wire is immediately negative; if the magnesium wires be not connected with the instrument till the black incrustation is gone, scarcely any electrical difference is then observed between them. Similar experiments can also be made with other conducting liquids; the process, however, is more intricate and furnishes no definite results, because hydrate of magnesia may be formed on both wires, which is not possible when dilute acids are employed.

The first idea which presented itself with regard to the participation of the suboxide in the development of hydrogen was, that the current only partly decomposed the salts of the solutions in the normal manner, and partly the water itself. If, for example,  $mH$  were given off from the cathode in a solution of chloride of sodium, and  $pH$  from the anode, the quantity of magnesium dissolved is, according to the experiments described,  $=(m+p)Mg$ . Let the current so divide itself that it decompose  $x$  equivalents of water, then  $xO$  and  $(m-x)Cl$  will be set free. The latter combines with  $(m-x)Mg$ , leaving  $(p+x)Mg$ , which forms an oxide with  $xO$ . When this compound has been completely oxidized to magnesia, it contains  $(p+x)MgO$ . If we could determine this quantity experimentally, we should also know  $x$ , the portion of the current that decomposes water. I examined therefore, first of all, whether the quantity of magnesia formed in the nascent state, in a salt liquid holding chloride of magnesium in solution, was considerable. 0.067 grm. of magnesium wire, equivalent to 62.6 cubic centims. of hydrogen, was placed under a eudiometer in a solution of common salt which had frequently been used for electrolysis with magnesium, until the wire had crumbled away to a white powder. The liquid was filtered off from the precipitate; the latter was washed on the filter, and then dissolved in dilute sulphuric acid. After evaporating this liquid, 0.328 grm. of sulphate of magnesia remained, which is equivalent to 0.0656 grm. of magnesium, or 61.1 cubic centims. of hydrogen. 62.5 cubic centims. of hydrogen had been given off. It is thus seen that no appreciable quantity of magnesia had been dissolved.

Solution of chloride of sodium was now decomposed between magnesium electrodes, and, after the black precipitate had been converted into the white powder, the above process repeated.

\* See my own researches, in Poggendorff's *Annalen*, vol. lxxvii. p. 504.



Two experiments gave the following results:—

Hydrogen. Found.	Sulphate of magnesia.	Hydrogen. Calculated.
39.9	0.209	39.06
25.9	0.132	24.7

According to this, the quantity of sulphate of magnesia was equivalent to the hydrogen evolved; that is to say,  $p+x=p$ , and consequently  $x=0$ . The black precipitate was therefore not produced by the action of the current, but by a purely chemical process.

The black incrustation nevertheless required the agency of the current for its formation. A bright magnesium wire, when placed in distilled water, is but feebly attacked; some hydrogen is developed, and a thin film of hydrate of magnesia covers the wire, protecting it from further change. It was not noticed that this oxidation is preceded by the formation of the suboxide. If the part not immersed be touched by a platinum wire, which likewise dips into the acid, the magnesium then becomes black; on stopping the current the incrustation dissolves. In a solution of chloride of sodium a magnesium wire long retained its metallic lustre; when touched with a platinum wire, as above described, it turns immediately black. Moreover, even without the use of platinum, black spots form on the wire, whence a black incrustation soon spreads over its entire surface. A copious quantity of hydrogen is now evolved from it. The first black spot is due to local currents arising from small inequalities of the surface: as soon as the first spot is formed, local currents of greater intensity are produced. But these currents do not, any more than that of the battery, decompose the water, but the salt in the solution; the part, therefore, which the current plays in the formation of the suboxide is no other than that of continually exposing fresh metallic surfaces to the action of the water.

The several phenomena which different salt solutions present are now easily to be explained. In chloride of ammonium, the suboxide dissolves immediately on its formation, with evolution of hydrogen, because magnesia is, as a rule, soluble in ammoniacal salts. In solution of chloride of sodium it changes, without being dissolved, into hydrate of magnesia, because chloride of magnesium forms no basic salt with magnesia. On the other hand, it dissolves to a certain degree, and with evolution of hydrogen, in sulphate of magnesium, because in this case a basic salt is generated. This basic compound appears to be formed when  $H_- : H_+$  as 3 : 1; hence we should be able to deduce the composition of this salt if that of the suboxide were known.

Wöhler and Buff ascribed the evolution of hydrogen from the

positive aluminium wire to the ready solubility of the basic chloride of aluminium. This, though undoubtedly a true cause, is not the sole one. It is to be presumed, from what has gone before, that the development of hydrogen from the aluminium and the magnesium has a common origin; besides, the positive aluminium wire also becomes black during electrolysis, and at the end of the process continues to give off hydrogen, like the magnesium wire, only not so abundantly. All the cases of electrolysis examined by Wöhler and Buff furnished a solution of basic chloride of aluminium; and it never occurred to them to investigate cases of a different kind, their interest being concentrated on the formation of siliciuretted hydrogen. If in place of a strong solution of chloride of sodium a dilute one be employed, the alumina is no longer completely soluble, and the experiment then bears a greater resemblance to that with magnesium. The wire not only turns black, but the whole of the liquid in the eudiometer becomes grey. A grey powder separates from the wire, and continues to evolve hydrogen after the electrolysis is interrupted. I have never seen it become entirely white. If washed on a filter and treated with dilute hydrochloric acid, it completely dissolves; it contained no silicium, or only trifling quantities, like the aluminium wire itself, which I obtained from the same source as the magnesium wire used in the foregoing experiments. The solution contained iron, however; and to this the grey colour may possibly have been due. The electrolysis observed by Wöhler and Buff with concentrated solution of chloride of sodium between aluminium wires corresponds therefore entirely to that, examined by me, of solution of sulphate of magnesium between magnesium electrodes; we ought consequently to find also in the latter case the nearly constant ratio of  $H_- : H_+$ . The electrolysis of dilute solution of common salt no longer gave this proportion; on the contrary, I invariably found the aluminium dissolved to be equivalent to two-thirds of the quantity of hydrogen given off from the two poles. I believe, therefore, that in the case of aluminium also the formation of a suboxide precedes the evolution of hydrogen. A peculiar circumstance prevents the separation of this suboxide. On account of the solubility of the basic chloride, no great quantity of the substance could be obtained either from dilute solution of chloride of sodium or from dilute hydrochloric acid. In other salt solutions and in dilute sulphuric acid, however, no evolution of hydrogen takes place; here, on the contrary, the phenomenon is that which has been already described by Buff\*. The positive aluminium wire becomes covered with a dark incrustation, which is strongly electro-negative and a very bad conductor; it gives off a little

\* *Ann. der Chem. und Pharm.* vol. cii. p. 269.

oxygen and no hydrogen; the current is so weakened that it is nearly reduced to *nil*. Buff regarded this incrustation as silicium. The formation of a coating of silicium is undoubtedly quite conceivable; for our aluminium always contains some. I have, however, a reason for not regarding this film as silicium: pour some silicium powder into a glass tube the lower end of which is closed with parchment paper; dip this end into dilute sulphuric acid; then place one aluminium wire in the acid and another in the silicium, and in every case the silicium is found to be *positive* towards the aluminium. It matters not in this experiment which of the wires be first dipped in the solution, the aluminium wire immersed in the acid is invariably negative. If the current be weak on account of the bad conducting-power of the silicium, it is only necessary to press the aluminium wire strongly against the powder in order to bring its particles more closely in contact with one another—a method previously adopted by me when using substances in a pulverized state\*. The silicium which I employed was crystalline. Amorphous silicium was not readily procurable at the time, though I had a body which comports itself in a precisely analogous manner—amorphous boron. This body, when treated in the same manner with aluminium wires, was also distinctly positive. The badly-conducting incrustation therefore could hardly be silicium; I regard it, on the contrary, as a suboxide of aluminium. At all events this suboxide is a very bad conductor, it consequently does not give rise to the formation of local currents; and it does not dissolve in dilute acids. If, on the other hand, from the possibility of forming basic salts, it be predisposed to further oxidation, it gives rise to just the same phenomena as the suboxide of magnesium; and consequently the explanation given by Wöhler and Buff, for the only case which concerns us here, of the anomalous formation of hydrogen is the correct one.

Buff† entertains the same view of the passive state of the metals which is upheld by me‡. He finds in a very insoluble layer of oxide or in a film of oxygen, protecting the metal from further attack, the cause of the passive state. The formation of a suboxide on the surface of a metal which is known to possess the property of passivity to a high degree, appears to me to give additional support to this view.

Henrici found, in his experiments on the effect of motion of metallic wires in liquids, that aluminium comports itself in a totally different way from other metals. In explanation of this anomalous behaviour, he says§, "If it be assumed that the alu-

\* Poggendorff's *Annalen*, vol. cxi, p. 619.

† *Ann. der Chem. und Pharm.* vol. cii. p. 265.

‡ Poggendorff's *Annalen*, vol. lxxvii. p. 186. § Ibid. vol. cxxi. p. 496.



minium, covered as it is with a thin, insoluble, oxidized film, becomes negatively excited in the immediate region by the hydrogen which is set free, whilst the film itself is preeminently positive towards the metallic surface that it overlies, then the phenomenon observed must undoubtedly make its appearance." I believe that my experiments have justified this assumption.

XXXV. *On a Problem in the Calculus of Variations, in reply to Mr. Todhunter.* By Professor CHALLIS, M.A., F.R.S., F.R.A.S.\*

I HAVE only a few concluding words to say respecting the problem in the Calculus of Variations, the consideration of which is resumed by Mr. Todhunter in the September Number, the discussion of it having advanced to a stage at which, so far at least as my views are concerned, a definite issue may be stated. I have all along understood the problem to be that which Mr. Todhunter has thus enunciated: To determine the greatest solid of revolution, the surface of which is given, and which cuts the axis at two fixed points. The generating line of the surface I suppose to be subject also to the condition of being continuous, so far as not to change its direction *per saltum*. It has been shown in the course of this discussion that different lines fulfilling this condition, together with that of *cutting* the axis at the two points, give solids having the same superficies but different degrees of magnitude. As these gradations cannot go on unlimitedly, there must be a limiting or maximum solid the surface of which fulfils the same conditions. It would be possible by practical tentative methods, although it would be an unscientific proceeding, to mould a given quantity of matter into the required form. The maximum, therefore, exists *in rerum naturâ*; and to the discovery of its form by analysis all my efforts have been directed. I cannot recognize as having any claim to be called the solution of the problem a form which does not fulfil the above conditions.

In the July Number I have given two investigations—one depending on the equation  $\Lambda p = 0$ , and the other on  $\Lambda = 0$ . I showed at the same time that the former equation could only give a line symmetrical with respect to the axis of revolution, and consequently, if any, only a conditional maximum, and that the absolute maximum must be deduced from the equation  $\Lambda = 0$ . Further, it was inferred from the radical involved in  $\Lambda$  (assuming always that the function or functions to be found admit of exact algebraic expression), that the equation  $\Lambda = 0$  should be resolved

\* Communicated by the Author.



into  $A'=0$  and  $A''=0$ , to meet the case of two ordinates to the same abscissa. The equation  $Ap=0$  did not require the same resolution, on account of its fulfilling the above-mentioned condition of symmetry. Having on these principles obtained, by processes which will be presently again adverted to, two solids of definite forms, I proceeded to apply tests to ascertain whether they were really maxima. It is well known that results given by the rules for finding maxima and minima must satisfy certain criteria before they can be pronounced to be solutions of the proposed questions. In default of general criteria, it is necessary in the Calculus of Variations to have recourse to tests by trial of particular instances. The tests I applied happened to accord with the supposition of maxima; and I concluded, it appears on insufficient grounds, that such was the character of the two forms. Mr. Todhunter, by a more skilful application of tests, has proved (in the September Number) that the forms in question are not maxima. Of course I admit without reservation that all the inferences I drew from the supposed maxima fall to the ground. By availing myself of this correction of my mistakes I have been enabled to arrive at some definite conclusions respecting the proper process for solving the problem, to which I shall direct attention after giving a few preliminary explanations.

Relative to the solution drawn from the equation  $A=0$ , Mr. Todhunter urges that "we have to satisfy *both*  $A'=0$  and  $A''=0$ ." This I conceive that I have done. I have employed integrals of these equations which may be written  $\int y'dx = M' + C'$  and  $\int y''dx = M'' + C''$ , the former of which satisfies  $A'=0$ , and the other  $A''=0$ , as is evident by simply differentiating them. Also the equations are thus satisfied by general or *indefinite* integrals, which is an indispensable condition. I next proceed to use these values of  $\int y'dx$  and  $\int y''dx$  strictly according to the indications of the analysis, always taking into account that  $y'$  and  $y''$  are ordinates to the same abscissa, and I obtain *definite* integrals between the values  $p = \text{infinity}$  and  $p = 0$ . The result is that the area cut off by the larger ordinate is equal to the length of the bounding curve multiplied by the constant  $\lambda$ . As that ordinate cuts the curve at right angles, this result indicates that the curve is a *circle* of radius  $\lambda$ . Every step of this process is legitimate if the next preceding step is legitimate; and therefore the legitimacy of the result depends on the equations  $A'=0$  and  $A''=0$  having been both satisfied. All this argument, however, presupposes that the equation of the curve admits of definite algebraic expression, the resolution itself into two equations being an operation performed on algebraic principles.

Up to this point the reasoning is the same as that in the July Number. The subsequent reasoning there proceeds on the assumption that the centre of the circle might be placed so as to make the curve pass through the given points. But Mr. Todhunter has pointed out that in that case the equation  $A=0$  is not satisfied. I find, in fact, on making the trial, that the equation is satisfied *only when the centre of the circle is on the straight line joining the two points*. Hence it follows that the line is a semicircle the extremities of which are coincident with the points. But this cannot be the case unless the given surface is equal to that of a sphere of which the interval between the points is a diameter; so that we have thus solved only a very restricted case of the general problem. It is to be observed that this result has been obtained by using exclusively the equation  $A=0$ , and therefore without assuming, as is done when the equation  $Ap=0$  is used, that the line is symmetrical with respect to the axis of revolution. Thus, considering the premises of the argument, we may conclude from it that, so far as is indicated by the equation  $A=0$ , the problem admits of no *exact algebraic solution* except the restricted one just mentioned.

With respect to the deductions I made from the equation  $Ap=0$ , I have ascertained that a logical fault was committed where I used the equation  $y=c$  instead of the equation  $y=0$ , the latter having been obtained by the integration of the complete differential equation  $Ap=0$ , and therefore not admitting of being superseded by integrating  $p=0$ . Also the before-mentioned condition of symmetry would seem to require that the straight line should be coincident with the axis of  $x$ . Having abandoned the solution depending on the equation  $y=c$ , I have no occasion to meet the objection that it did not satisfy  $A=0$  as well as  $Ap=0$ ; but the present argument necessitates the remark that this objection remains valid against the solution which Mr. Todhunter advocates in the Magazine for June, viz. that in which the required line consists partly of a straight line coincident with the axis, and partly of a semicircle. He himself shows that, so far as regards the straight line,  $A=2\lambda$ , and then proceeds to meet the difficulty by arguing *à posteriori* that at any rate a maximum is obtained. Without denying the truth of this conclusion, I assert that the difficulty is in this way evaded rather than met and overcome. The real explanation may, I believe, be derived from the result of the foregoing discussion of the equation  $A=0$ . It is there shown that that equation is satisfied by no definite algebraic integral fulfilling the condition of a maximum. This being the case, suppose that we have obtained from the equation  $Ap=0$  a definite algebraic solution; this solution cannot satisfy  $A=0$  *throughout*; for if so, the latter equa-

tion would be compatible with a definite algebraic solution, which is contrary to what was before proved. Thus, under the circumstances of this problem,  $\Delta p = 0$  and  $\Delta = 0$  are not equivalent equations, only the former admitting of an exact form of solution; on which account I still think I am right in calling the solution a *conditional* maximum, the condition in this instance being that the line be symmetrical with respect to the axis of  $x$ . There can be no question that a maximum is in this manner really obtained, if only for the reason that of all solids, regular or irregular, of given surface, the sphere is the greatest; but evidently the maximum we are in search of must not be subjected to that condition. It may also be noticed that the solution, since it gives a *discontinuous* line, is analogous to that of the problem of the shortest course of a ship, and confirmatory of the principle that the Calculus of Variations is comprehensive of discontinuous solutions.

I can see no good reason for the attempt (in the September Number) to show that "a figure formed of an arc of a semicircle and a straight line which coincides in direction with the bounding diameter" may be regarded as a continuous figure, nor do I perceive what bearing this idea has on the treatment of the problem. What objection can there be to the common-sense view that such a figure is discontinuous? Also I cannot forbear noticing what strikes me as an inconsistency, where, at the close of his communication, Mr. Todhunter first expresses the opinion that the use of the equation  $\Delta p = 0$  may be dispensed with, and then states that he accepts, as the only true solution of the problem, one which is actually derived from the equation  $\Delta p = 0$ , and is not derivable from the equation  $\Delta = 0$ . It cannot but be a right rule of analysis, to regard as non-equivalent expressions symbolically distinguished.

The following are the conclusions I have come to from this reconsideration of the question:—

(1) The Calculus of Variations furnishes no other solution in *definite algebraic form* than that which gives for the generating line of the surface a discontinuous line, consisting partly of a semicircle and partly of a straight line coincident with the axis. But this solution does not satisfy the conditions of cutting the axis at the given points, and of continuity of form.

(2) In order to satisfy those conditions, it is necessary to integrate the equation  $\Delta = 0$  by successive approximations; which being done, the value of  $y$  is obtained in a series which is not the development of a definite algebraic function of  $x$ .

The form of the surface might thus be obtained for different sets of numerical values of the constants. I do not know what difficulties would be met with in the attempt to effect such ap-



proximate integrations, but I do not apprehend that they would be insuperable.

For the sake of further illustration of the principles of the Calculus of Variations, I propose to conclude with some remarks on a problem similar to the one that has been under discussion, but not to be confounded with it. Let it be required to find the greatest solid of revolution of given superficies, the generating line of the surface consisting of ordinates perpendicular to the axis at two given points, and of a curve connecting them. Mr. Todhunter proposed this problem in p. 410 of his 'History of the Calculus of Variations,' and in all essential points effected the solution of it by proving that the curve must join on continuously with the ordinates, and that the ordinates must be equal. In the Philosophical Magazine for August 1861, I found that the relation between the ordinate  $y$  and the length  $s$  of the curve could be thus expressed:

$$\cos\left(\frac{s}{a} + k\right) = \frac{2a^2 + b - y^2}{2a\sqrt{a^2 + b}},$$

$2a$  being what I have hitherto called  $\lambda$ , and  $k$  and  $b$  arbitrary constants introduced by the integrations. MM. Delaunay and Sturm had proved (*Journal de Liouville*, vol. vi. p. 315) that the curve to which this equation belongs may be described by the focus of an hyperbola rolling on a straight line, the latter mathematician discussing it with reference to the problem treated of in the previous part of this communication. But what I chiefly wish to remark is, that although the above equation was obtained by the integration of the equation  $Ap=0$ , it satisfies the equation  $A=0$ —that is, the equation

$$y + a\sqrt{1+p^2} - \frac{d}{dx} \frac{ayp}{\sqrt{1+p^2}} = 0,$$

as might easily be verified. Hence the factor  $p$  has no such significance here as in the former problem, and the curved line is altogether continuous. In the March Number of this year, I have called in question the truth of this solution; but as this was done in consequence of the error I had fallen into relative to the integral of the equation  $A=0$ , as already pointed out, I beg to withdraw what I have there said. I see now no reason to doubt that the form of the curve above mentioned is the true solution, although it might be difficult to apply a test. For the particular case in which  $b=0$ , and therefore  $k=0$ , the curve is a semicircle terminating at the two points; and thus this result coincides with that restricted solution of the former problem which was deduced from the equation  $A=0$ , as it manifestly



should. In this second problem a nearer approach is made to a definite algebraic solution than in the other; but as the relation between  $x$  and  $y$  is not deducible by integration from that between  $s$  and  $y$ , the value of  $y$  as a function of  $x$  can only be obtained in a series which is not a development of a definite algebraic expression.

Cambridge, September 18, 1866.

### XXXVI. On *Molecular Physics*. By Prof. W. A. NORTON.

[Concluded from p. 212.]

#### *Chemical Action.*

THE general nature of the process of combination of two dissimilar molecules has already been considered (vol. xxx. p. 109). We must now contemplate it more in detail, and take note of certain distinctions and possible differences of result. We have seen that two dissimilar molecules have an affinity for each other when their unequal molecular forces are so related that under their mutual action the atmospheres become polarized—that is, the electric æther accumulates upon one of the two contiguous sides, and is partly expelled from the other, so that the former will be positive and the latter negative. The attraction that results from this disturbance of the electric equilibrium constitutes, as we conceive, the proper *force of affinity* or *chemical attraction*. It ordinarily comes into operation beyond the outer limit of the molecular attraction proper (*i. e.* beyond  $Oc$ , fig. 1, p. 203, vol. xxviii.), and draws the particles nearer together until they come within the range of this attraction, which then determines their complete and permanent union. The force of electrical attraction or affinity thus brought into play should ultimately diminish, if not pass off entirely, by reason of the electric discharge that would ensue between the particles. Heat or the electric spark may increase the natural force of affinity by augmenting the natural polarization that the molecular forces may have initiated. In fact all the various circumstances upon which the union of two dissimilar molecules depends are but so many different circumstances under which the molecules become polarized by their natural mutual action more or less modified.

We have seen (vol. xxx. p. 99) that a compound molecule, when formed, becomes invested with its own proper atmosphere, and so comes into special relations with other molecules, whether simple or compound, similar or dissimilar. The density and extent of such an atmosphere may vary widely with the degree

of approximation of the elementary particles and other particulars.

*The relations of heat to chemical phenomena* may be deduced from the principles already stated. The heat of combination results from the condensation of the electric æther that takes place between the uniting particles, and from the compression of their individual electric atmospheres—one or both of these effects. Both of these effects should give rise to an emission of universal æther in heat-pulses.

But, according to Favre and Silbermann, certain substances combine with an attendant absorption instead of an evolution of heat. To understand how this may happen, we must observe that, according to the received ideas of the true nature of chemical processes, the molecules of all substances are composed of two or more atoms associated together; and when two substances combine, it generally happens that one or both of the two molecules presented to each other is decomposed, and two new compound molecules are formed by condensation. Now the decomposition that precedes the combination should occasion a loss of heat by reason of the expansion of the electric æther condensed between the constituent molecules (or “chemical atoms”), and of the atmospheres of these molecules; and the subsequent combination by the reverse process should develop heat. If the loss of heat from the one cause exceeds the gain from the other, there will be an effective absorption of heat as the result of the combination. On the other hand, when chemical combination occasions an evolution of heat, it is in general because the heat absorbed while the decomposition of individual molecules is going on, is afterwards more than restored by the heat developed in the combination that succeeds the decomposition. Thus when oxygen and hydrogen combine to form water, heat is evolved because, as we conceive, much less heat is lost in the decomposition of the binary molecule of oxygen than is produced in the union of the two separated molecules (chemical atoms) of oxygen, each with a molecule of hydrogen. In some instances, as in the formation of the hydrate of lime, the molecules would seem to combine without any previous decomposition, and any tendency, therefore, to absorption of heat. In the decomposition of substances, as well as in their combination, it is found that heat may either be absorbed or evolved. This fact admits of a similar explanation to that just given. M. Schröder Van der Kolk, in a memoir “On the Mechanical Energy of Chemical Action,” a translation of which is given in the April Number of the *Philosophical Magazine* (1865), lays down the following law of decomposition:—“Bodies which evolve heat in being decomposed by heat are not again formed in the

subsequent cooling." According to what has just been stated, all such bodies must evolve heat because of the electric condensation that attends the formation of new compound molecules after the primitive molecules have been decomposed. Now, if these new molecules be cooled, the tendency would be to increase the molecular attraction by which their constituents are held together, rather than to favour their decomposition. The instances cited, viz. protoxide of nitrogen, peroxide of hydrogen, chlorous and chloric acids, the chloride, iodide, and sulphide of nitrogen, seem to sustain this explanation.

It is frequently found by experiment that if heat is absorbed in the act of decomposition, the separated components will reunite on cooling. It is probable that in such instances there is no formation of new molecules following the first decomposition, and that the heat which may be absorbed in addition to that consumed in the act of separation, is due solely to an expansion taking place after the receding molecules have been urged beyond the limit of molecular attraction and become subject to molecular repulsion. In that event a subsequent cooling, by contracting the atmospheres of the molecules and so increasing their attractive force, might favour a reunion. Hydrate of lime may be cited as a case admitting of this explanation.

We have seen that heat, by expanding and augmenting the repulsive energy of molecular atmospheres, tends virtually to polarize a surface positively, and that in this fact we have the probable origin of thermo-electricity (*l. c.* p. 276), and the explanation of the effect of heat in the development of electricity by friction (*l. c.* p. 108). The same polarizing action of heat should favour the oxidation of metallic surfaces. The condensing action of platinum and certain other metals upon gases, and of surfaces generally upon aqueous vapour with evolution of heat (see Silliman's *American Journal*, vol. xxxviii. p. 109), may be referred to a polarization developed by the mutual action of the surface and the gas or vapour. The attraction thus resulting, we must suppose, is not in general sufficient to bring the gases within the range of the natural molecular attraction, and so into complete union with the surface.

*Combination by Volume.*—The assumption is now generally made, that the molecules of all substances in the gaseous state occupy the same volume. This conclusion, to which chemists have been conducted, implies that there are the same number of molecules in equal volumes of different substances, and therefore that the elastic tension of the individual molecules is the same for all gases. This result corresponds with the determination of the repulsive energy of molecules at the greater distances, as given in Table I. (vol. xxviii. p. 200), if we regard the coefficient  $m$  as con-



stant, whatever may be the value of  $r$ . In fact the value of  $m$  depends upon the pressure to which the molecular atmospheres are exposed (vol. xxx. p. 99, foot-note) ; and this, in gases, must depend mainly upon the barometric pressure, and be constant for the same pressure. It is to be observed that the results given in Table I. hold good for compound molecules, provided as they are with their own especial atmospheres (*l. c.* p. 99), as well as for simple molecules. If  $r$ , the radius of the atmosphere of the mole-

cule, be increased in any ratio, the value of  $k \left( = \frac{m}{r^2} \right)$  will be dimi-

nished in proportion to the square of this ratio ; but if we estimate the force at a given distance, this distance, as expressed in terms of  $r$ , will be diminished in the same ratio that  $r$  is increased ; and hence, if the force varies inversely as the square of the distance, its value at the given distance will be the same as before. The elastic force of molecules posited at the same distance from each other should therefore be the same, whatever may be the radius  $r$  of the molecule, simple or compound. This result depends upon the assumption that the force of molecular repulsion varies, beyond a certain limit, inversely as the square of the distance. Table I. shows that for the smaller values of the ratio

$\frac{n}{m}$  (which should be taken for liquids that furnish vapours, and substances that habitually exist in the gaseous form) we have nearly reached this limit at the distance  $80r$ .

To this it should be added that the calculations are made upon the supposition that the ratio  $\frac{n}{m}$  remains constant for each set of computations, answering to each special value of  $\frac{n}{m}$ . But as a

matter of fact, in the transition from the liquid to the vaporous state, as we have seen (vol. xxviii. p. 282), the molecular atmospheres expand, which should diminish the value of  $n$ , and of the ratio  $\frac{n}{m}$ .

Accordingly, to represent truly the vaporous state, it is probable that the calculations should be made for a smaller value of  $\frac{n}{m}$

than any of those given at the head of the Table. If this be true, the limit above referred to may be greatly reduced. This should be the case especially with the permanent gases. The distinction between the gases and vapours lies in all probability in the fact of a smaller value of  $\frac{n}{m}$  for the former than the latter,

in consequence of which, compression or reduction of tempera-



ture of the permanent gases does not increase this value to the limit (4.93) at which the liquid state becomes possible.

The received theory among chemists, of combination by volume, is in entire accordance with these results derived from our theory of molecular forces, and with the conception to which we have been led of the constitution of simple and compound molecules (vol. xxx. p. 98, &c.). If we suppose, with the chemists, that in general the ultimate molecule is composed of two "atoms," this is equivalent to saying, in the language of the present theory, that the ultimate molecule is a compound molecule consisting of two simple molecules united together, and provided with its own proper atmosphere.

All such binary molecules of elementary gases will occupy, as we have seen, the same space, which may be called the unit of volume. If  $v$  represent any given volume, as a cubic inch, and  $n$  the number of atoms in  $v$ , then this unit of volume will be  $\frac{v}{n}$ . Now, if one volume of one gas be presented to one volume of another, the general result is that two volumes of a compound gas are formed. This implies that each of the binary molecules is decomposed, each atom of the one combines with one of the other, and thus two new compound molecules are formed, each occupying one unit of volume. If, as in the formation of carbonic acid, one volume of one gas unites with one volume of another, and one volume of compound gas is formed, we must suppose that the two binary molecules unite, as wholes, and form one new molecule containing four atoms associated in pairs. Again, if, as in the formation of aqueous vapour, two volumes of one gas combine with one of the other, and two volumes are formed, we now have two molecules  $a$  and  $b$  combining with one,  $c$ ;  $c$  must be decomposed, and one of its atoms must combine with  $a$ , and another with  $b$ : thus each molecule of water contains two atoms of hydrogen, associated with one atom of oxygen. If, as in the production of ammonia, three volumes unite with one, and two volumes are produced, three molecules must combine with one and two new compound molecules result. This implies that the single molecule and one of the three molecules are decomposed, and that the disunited atoms combine with the other two. If the molecules of the two gases, or vapours, that combine be ever so complex, and the same number of volumes unite as we have above supposed, with the same result as to the number of volumes produced, the processes will be essentially the same as just indicated. Each compound molecule will occupy one unit of volume, whatever number of atoms, or groups of atoms, it may contain.

The decomposition of molecules which occurs in such cases

must be attributed to the molecular polarization that precedes and accompanies the act of combination, in conjunction with, under special circumstances, the exertion of a separating force due to heat, light, or an electric current. We have seen already, in considering the process of decomposition of a molecule of water by the chemical action of zinc (vol. xxx. p. 110), that such action upon one of the elements of a binary compound tends to separate it from the other, if the two are in conducting communication—as they would be in every true compound molecule, by reason of the electric æther condensed between them.

*Chemical Action of the Actinic Rays.*—We understand by the actinic rays, the solar rays of high refrangibility, which are capable of producing chemical effects entirely distinct from the effects of heat. From the view we have taken of the origin of rays of heat and light (vol. xxviii. p. 430 &c.), we are led to conceive of all the solar radiations as essentially of the same nature, and differing only in the rapidity of vibration and in the intensity of the impulses propagated in the ray, and that they owe these differences to the fact that they originate in the vibrations of the atomettes of molecular atmospheres posited at various distances from the central atoms of the molecules (*l. c.* p. 430). The most refrangible actinic rays should then emanate from the atomettes that lie at the greatest distances from these atoms.

The chemical action of light, and of the actinic rays in general, appears to be a consequence of the feeble repulsive individual impulses propagated in the rays that originate in the upper portions of molecular atmospheres. Such feeble impulses cannot penetrate far into the molecular atmospheres upon which they fall, and must pass around them. They should accordingly tend to urge a portion of the electric æther that may lie in their route around to the further side of the molecule, and so to bring it into a state of positive electrization. The nature of the action that will ensue in consequence, upon the next molecule beyond that which receives the ray, must depend upon whether there is an electric conducting connexion between the two or not. If there be such connexion, the tendency of the action of the free electricity set in motion will be to separate or decompose the two molecules, which, in the case supposed, will be chemically united. The action here considered is essentially the same as that which occurs in the decomposition of water by zinc (vol. xxx. p. 110). Most cases of the chemical action of light would seem to be explicable upon this idea. Thus, we may explain the action of light upon an explosive mixture of chlorine and hydrogen by the decomposition of the elementary molecules of the two gases, and the resulting formation of two molecules of hydrochloric acid. The reduction of the chloride of silver to a subchloride by

the action of light might result from the same general tendency to effect a decomposition of united molecules.

Heat may in some cases produce the same chemical result as light, or the actinic rays generally. For example, it explodes the mixture of chlorine and hydrogen. But the effect must be ascribed to the repulsive action of the heat-pulses taken up by the molecular atmospheres at considerable depths below their surface; whereas the separating action of the actinic rays is probably due to a movement of the electric æther effected at the surface of the atmospheres. It is questionable whether the actinic rays are capable of imparting any sensible polarization to molecules. In this respect their tendency is the reverse of that of heat, viz. to impart a negative instead of a positive polarity; for their impulses act directly upon the æther of the molecular atmospheres, but the heat-impulses, as we have seen, act indirectly, producing expansion. The distinction is the same, essentially, as that taken between the two modes of action of the external impulses exerted by electric currents (*l. c.* p. 280),—the one, analogous to light, developing magnetic currents in groups of molecules, and the other, like heat, determining a reverse polarization of molecules, compound or simple, by an indirect expansive action.

XXXVII. *On the Origin of Muscular Power.*

By Professor C. MATTEUCCI.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

Royal Institution,  
September 24, 1866.

I BEG to forward you the enclosed letter just received from Professor Matteucci. It will doubtless be read with attention by many who are now interested in the discussion of this subject.

I am, Gentlemen,

Yours truly,

E. FRANKLAND.

Firenze, September 9, 1866.

DEAR PROFESSOR FRANKLAND,—The lively interest which I felt in reading your memoir “On the Origin of Muscular Power,” forming the sequel of the beautiful experiments of Professors Fick and Wislicenus, induces me to remind you of some conclusions which I drew, a few years ago, from my electro-physiolo-

*Phil. Mag.* S. 4. Vol. 32. No. 216. Oct. 1866.

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gical investigations, and which appear to me to contribute at the present moment towards the completion of our knowledge on this important part of animal physics.

In the first place I may remark, in reference to the Table of results of Dr. E. Smith's investigations on the quantity of carbonic acid exhaled during rest, and during the muscular exertion of man in various kinds of work, that it may be of service, as regards the conclusion which it is sought to draw from these results, to call to mind some experiments of mine upon the exhalation of carbonic acid, by muscles *deprived of blood*, during repose and during contraction. I believe, in fact, that in the experiments of Dr. E. Smith, the greater part of the carbonic acid exhaled is derived from the carbonic acid dissolved in the blood, and which is exhaled in abundance owing to the greater activity of the work of respiration during exercise; whilst, on the other hand, in the muscles of frogs prepared as in my experiments, the greater part of the carbonic acid which is given off by those muscles during contraction must be attributed to the oxidation of the muscular matter, or of the substances which are mixed with it. I may add that in recently repeating, with the same results, these experiments on the muscles of frogs which had been washed several times in water, it appeared to me that, whilst entirely admitting the accuracy of your conclusions, and of those drawn from the experiments of Fick and Wislicenus, one cannot avoid conceding that the muscular fibre itself is also oxidized and burnt during contraction.

You say in your memoir, "a command is sent from the brain to the muscle, the nervous agent determines oxidation; the potential energy becomes actual energy, &c." On this part of the subject I wish to mention a conclusion drawn rigorously from experiment, and which throws much light precisely upon this point. It is easy to imagine an experiment in which the crural nerve of a prepared frog is excited by the interrupted passage of an electric current, whilst the work of the muscle thrown into contraction by this excitation is determined in metrekilograms. This experiment is doubtless not free from error, which, however, operates in the same direction, viz. to diminish the total muscular work developed by the muscular contraction. In fact it is known that there are muscles which, in the sum total of contractions, act to diminish the height to which the little weight attached to the leg is lifted. I have proved that there is also heat developed by the contraction of muscles deprived of blood. I repeat, then, the work calculated from the lifting of a weight, and the height to which it is lifted, is certainly inferior to the total work of muscular contraction. On the other hand, however, whilst employing the most feeble



electric current possible to excite contraction, it is easy to determine the quantity of zinc oxidized in the battery during the passage of the current which is employed to excite the nerve and produce contraction. Whatever may be the theoretical, or rather hypothetical idea which is formed, as to the manner in which the electric current acts upon the nerves, it is impossible to deny that there exists some connexion between the quantity of zinc oxidized in the battery and measured in the voltameter, the electric current thus obtained, and the corresponding nervous excitation produced. It results, from a great number of experiments of a kind admitting of no uncertainty, that *the work produced by muscular contraction is enormously greater than the corresponding chemical or calorific work in the battery*. It necessarily follows from this, that the nervous irritation cannot act without having previously given rise to the combustion of the organic matters, azotized or non-azotized, which accompanies muscular contraction.

I have still to add a remarkable relation between these phenomena and the electromotive force of the muscles. It may be illustrated by one of the most beautiful and certain of electrophysiological experiments, which consists in closing the circuit of the galvanometer with two equal and opposed muscles, such as the two half-thighs (*demi-cuisses*) of a frog, which touch each other by the two interior sections. There is no current perceptible to the galvanometer when the preparation is well made. If contraction be now produced in one of the half-thighs several times in succession, and the circuit be closed after as before, there is obtained a very marked differential current, the direction of which indicates the superiority of the electromotive force of the muscle left at rest. It may be here remarked that this result cannot be explained by attributing it to the acid which may be supposed to be set free by the contraction; for on this hypothesis the differential electric current would be in the opposite direction to that which is actually observed. We are therefore driven to the conclusion that during muscular contraction there are such chemical changes in operation as weaken the electromotive force of the muscle.

Believe me, yours truly,

C. MATTEUCCI.

XXXVIII. *Sixth Memoir on Radiation and Absorption—Influence of Colour and Mechanical Condition on Radiant Heat.* By Professor J. TYNDALL, LL.D., F.R.S., &c.\*

FRANKLIN placed cloths of various colours upon snow and allowed the sun to shine upon them. They absorbed the solar rays in different degrees, became differently heated, and sank therefore to different depths in the snow beneath them. His conclusion was that dark colours were the best absorbers, and light colours the worst ; and to this hour we appear to have been content to accept Franklin's generalization without qualification. In my last memoir I briefly pointed out its probable defects. Did the emission from luminous sources consist exclusively of visible rays, we might fairly infer from the colour of a substance its capacity to absorb the heat of such sources. But the emission from luminous sources is by no means all visible. In terrestrial sources by far the greater part, and in the case of the sun a very great part, of the emission consists of invisible rays, regarding which colour teaches us nothing.

It remained therefore to examine whether the results of Franklin were the expression of a law of nature. Two cards were taken of the same size and texture ; over one of them was shaken the white powder of alum, and over the other the dark powder of iodine. Placed before a glowing fire and permitted to assume the maximum temperature due to their position, it was found that the card bearing the alum became extremely hot, while that bearing the iodine remained cool. No thermometer was necessary to demonstrate this difference. Placing, for example, the back of the iodine card against the forehead or cheek, no inconvenience was experienced ; while the back of the alum card similarly placed proved intolerably hot.

This result was corroborated by the following experiments :— One bulb of a differential thermometer was covered with iodine, and the other with alum powder. A red-hot spatula being placed midway between both, the liquid column associated with the alum-covered bulb was immediately forced down, and maintained in an inferior position. Again, two delicate mercurial thermometers had their bulbs coated, the one with iodine, the other with alum. On exposing them at the same distance to the radiation from a gas-flame, the mercury of the alum-covered thermometer rose nearly twice as high as that of its neighbour. Two sheets of tin were coated, the one with alum, and the other with iodine powder. The sheets were placed parallel to each other, and about 10 inches asunder ; at the back of each was

\* From the Philosophical Transactions for 1866, Part I.

soldered a little bar of bismuth, which with the tin plate to which it was attached constituted a thermo-electric couple. The two plates were connected together by a wire, and the free ends of the bismuth bars were connected with a galvanometer. Placing a red-hot ball midway between both, the calorific rays fell with the same intensity on the two sheets of tin, but the galvanometer immediately declared that the sheet which bore the alum was the most highly heated.

In some of the foregoing cases the iodine was simply shaken through a muslin sieve; in other cases it was mixed with bisulphide of carbon and applied with a camel's-hair brush. When dried afterwards it was almost as black as soot; but as an absorber of radiant heat it was no match for the perfectly white powder of alum.

The difficulty of warming iodine by radiant heat is evidently due to the diathermic property which it manifests so strikingly when dissolved in bisulphide of carbon. The heat enters the powder, is reflected at the limiting surfaces of the particles, but it does not lodge itself among the atoms of the iodine. When shaken in sufficient quantity on a plate of rock-salt and placed in the path of a calorific beam, iodine cuts the latter off. But its opacity is mainly that of a white powder to light; it is impervious, not through absorption, but through internal reflexion. Ordinary roll sulphur, even in thin cakes, allows no radiant heat to pass through it; but its opacity is also due to repeated internal reflexion. The temperature of ignition of sulphur is about  $244^{\circ}$  C.; but on placing a small piece of the substance at the focus of the electric lamp, where the temperature was sufficient to heat platinum-foil in a moment to whiteness, it required exposure for a considerable time to fuse and ignite the sulphur. Though impervious to the heat, it was not adiathermic. The milk of sulphur was also ignited with some difficulty. Sugar is a much less inflammable substance than sulphur, but it is a far better absorber; exposed at the focus, it is speedily fused and burnt up. The heat moreover which is competent to inflame sugar is scarcely competent to warm table-salt.

A fragment of almost black amorphous phosphorus was exposed at the dark focus of the electric lamp, but refused to be ignited. A still more remarkable result was obtained with ordinary phosphorus. A small fragment of this exceedingly inflammable substance could be exposed for twenty seconds without ignition at a focus where platinum was almost instantaneously raised to a white heat. Placing a morsel of phosphorus on a plate of rock-salt and holding it before a glowing fire, it bears, as proved by my assistant, Mr. Barrett, an intense radiation without ignition; but laid upon a plate of glass and similarly exposed, the phos-



phorus soon fuses and ignites; its ignition, however, is not entirely due to radiant heat, but mainly to the heat imparted to it by the glass\*.

The fusing-point of phosphorus is about  $44^{\circ}$  C., that of sugar is  $160^{\circ}$ ; still at the focus of the electric lamp the sugar fuses before the phosphorus. All this is due to the diathermancy of the phosphorus: a thin disk of the substance placed between two plates of rock-salt permits of a copious transmission. This substance therefore takes its place with other elementary bodies as regards deportment towards radiant heat.

The more diathermic a body is, the less it is warmed by radiant heat. No perfectly transparent body could be warmed by purely luminous heat. The surface of a vessel covered with a thick fur of hoar frost was exposed to the beam of the electric lamp condensed by a powerful mirror, the beam having been previously sent through a cell containing water; the sifted beam was powerless to remove the frost, though it was competent to set wood on fire. We may largely apply this result. It is not, for example, the luminous rays but the dark rays of the sun which sweep the snows of winter from the slopes of the Alps. Every glacier-stream that rushes through the Alpine valleys is almost wholly the product of invisible radiation. It is also the invisible solar rays which lift the glaciers from the sea-level to the summits of the mountains; for the luminous rays penetrate the tropical ocean to great depths, while the non-luminous ones are absorbed close to the surface, and become the main agents in evaporation.

It is often stated, without limitation, that ether might be exposed at the focus of a concave mirror without being sensibly heated; but this can only be true of a sifted beam. At the focus of the electric lamp, not only ether, but alcohol and water are speedily caused to boil, while bisulphide of carbon, whose boiling-point is only  $48^{\circ}$  C., cannot be raised to ebullition. In fact exposure for a period sufficient to boil alcohol or water is scarcely sufficient to render bisulphide of carbon sensibly warm.

If any one point came out with more clearness than any other in my experiments on gases, liquids, and vapours, it was the paramount influence which chemical constitution exerted upon the phenomena of radiation and absorption. And, seeing how little the character of the radiation was affected by the change of a body from the state of vapour to the state of liquid, I held it to be exceedingly probable that even in the solid state chemical constitution would exert its power. But opposed to this con-

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\* I believe this deportment of phosphorus towards radiant heat is not unknown to chemists.



clusion we had the experiments of Melloni on chalk and lamp-black, and the far more extensive ones of Masson and Courtépée on powders, which seemed clearly to show that in a state of extremely fine division, as in chemical precipitates, the radiant and absorbent powers of all bodies are the same. From these experiments it was inferred that the influence of physical condition was so predominant as to cause that of chemical constitution to disappear\*.

A serious oversight, however, seems to have connected itself with all the experiments of these distinguished men. Melloni mixed his lampblack and powdered chalk with gum or glue, and applied them by means of a camel's-hair brush on the surfaces of his radiating tube. Masson and Courtépée did the same. Melloni, it is true, thus compared a black surface with a white one; but the surfaces were seen to be white and black *through* the transparent gum, which in both cases was the real radiator. The same remark applies to Masson and Courtépée. Every particle of the precipitates they employed was a varnished particle; and the constancy they observed was, I imagine, due to the fact that the main radiant in all their experiments was the substance employed to make their powders cling to the surfaces of their cubes.

Gum or glue is a powerful radiator—in fact, equal to lamp-black; and it is a correspondingly powerful absorber; the particles surrounded by it had therefore but small chance of radiating through it. I sought to remedy this by the employment of a diathermic cement. Sulphur is highly diathermic; it dissolves freely in bisulphide of carbon; and at the suggestion of a chemical friend I employed it to fix the powders. The cube was laid upon its side, the surface to be coated being horizontal, and the bisulphide, containing the sulphur in solution, was poured over the surface. Before the liquid film had time to evaporate, the powder was shaken upon it through a muslin sieve. The bisulphide passed rapidly away in vapour, leaving the powder behind imbedded in the sulphur cement. Each powder, moreover, was laid on sufficiently thick to prevent the sulphur from surrounding its particles. This, though not perhaps a perfect way of determining the radiation of powders, was at all events an improvement on former methods, and yielded different results.

Ten or twelve cubes of tin were employed in the investigation. One side of each of them was coated with milk of sulphur, and this substance running through the entire series of cubes enabled me to connect the results of all of them together. The cubes

\* Masson and Courtépée, *Comptes Rendus*, vol. xxv. p. 938; Jamin, *Cours de Physique*, vol. ii. p. 289.

were heated with boiling water, and placed in succession at the same fixed distance in front of the thermo-electric pile, which as usual was well defended from air-currents and other extraneous sources of disturbance. Before giving the complete table of results, I will adduce a few of them, which show in a conclusive manner that in solid bodies radiation is molecular rather than mechanical.

The biniodide of mercury and the red oxide of lead resemble each other physically, both of them being of a brilliant red. Chemically, however, they are very different. Examined in the way indicated, their relative powers as radiators were found to be as follows:—

Name.	Chemical formula.	Radiation.
Biniodide of mercury .	(Hg I <sup>2</sup> )	39·7
Red oxide of lead . .	(2Pb O, Pb O <sup>2</sup> )	74·1

Mixed with gum and applied with a camel's-hair brush to the surfaces of the cube, the radiation from the following two substances fell out thus:—

Name.	Radiation.
Binoxide of mercury . . . . .	80·0
Red oxide of lead . . . . .	80·0

Here the influence of the gum entirely masks the difference due to molecular constitution.

The effect of atomic complexity upon the radiation is well illustrated by the deportment of these two substances. It is further illustrated by the deportment of two different iodides of mercury:—

	Radiation.
Biniodide of mercury (Hg I <sup>2</sup> ) . . . .	39·7
Iodide of mercury (Hg <sup>2</sup> I <sup>2</sup> ) . . . .	46·6

Here the addition of a second atom of mercury to the molecule of the biniodide raises the radiation 7 per cent. The experiment furnishes a kind of physical justification of the practice of chemists in regarding the molecule of yellow iodide of mercury to be Hg<sup>2</sup> I<sup>2</sup>, and not Hg I.

The peroxide and protoxide of iron gave the following results:—

	Radiation.
Peroxide of iron . . . . .	78·4
Protoxide of iron . . . . .	81·3

I did not expect this, the protoxide being a less complex molecule than the peroxide. On examination, however, the protoxide was found to be in part the magnetic oxide. The formulæ of the two substances are Fe<sup>2</sup> O<sup>3</sup> and Fe O, Fe<sup>2</sup> O<sup>3</sup>, and the anomaly therefore disappears.

Amorphous phosphorus and sulphide of iron gave the following results:—

	Radiation.
Amorphous phosphorus . . . .	63·6
Sulphide of iron . . . .	81·7

Sugar and salt were reduced in a mortar to the state of exceedingly fine powders. In point of cohesion and physical aspect these substances closely resemble each other; their radiative powers, however, are as follows:—

	Radiation.
Salt . . . .	35·3
Sugar . . . .	70·0*

In his last, interesting paper on emission at a red heat†, M. Desains mentions oxide of zinc as a body which at 100° C. has the same emissive power as lampblack. This is nearly true for the hydrated oxide; with the calcined oxide the following is the relation:—

	Radiation.
Lampblack . . . .	84·0
Hydrated oxide of zinc . . . .	80·4
Calcined . . . .	53·2

Two red powders have been already compared together; I will now compare two black ones. With black platinum and black oxide of iron the following results were obtained:—

	Radiation.
Black platinum (electrolytic) . . . .	59·0
Black oxide of iron . . . .	81·3

The black platinum here employed was obtained by electrolysis, a sheet of platinum-foil being coated with the substance.

Let us now compare two white powders. Chloride of silver and carbonate of zinc gave the following results:—

	Radiation.
Chloride of silver . . . .	32·5
Carbonate of zinc . . . .	77·7

As in all the other cases, the influence of chemical constitution makes its appearance here.

When held upon its cube by the sulphur cement, the chloride of silver soon darkens in the diffuse light of the laboratory. It first becomes lavender, and passes through various stages of

\* I have of course no intention of adducing experiments on sugar and salt, or on powdered rock-salt and alum, as opposed to the results of Masson and Courtépée. They would regard their results as unaffected by such experiments. It is the deportment of the *chemical precipitates* employed, and not that of bodies reduced to powder by mechanical means, that invalidates their conclusions.

† *Comptes Rendus*, July 3, 1865; *Phil. Mag.* August 1865.

brown to black. During these changes, which may be associated with a chemical reaction between the chloride of silver and the sulphur in which it is imbedded, the radiation steadily augments. Beginning in one instance with a radiation of 25, the chloride ended with a radiation of 60.

We have thus far compared two red surfaces, two black surfaces, and two white surfaces together. The comparison of a black and white surface gave the following result :—

	Radiation.
Black platinum . . . . .	59·0
White hydrated oxide of zinc . . . . .	80·4

Here the radiation from the white body far transcends that from the black one.

Again comparing black and white, we have the following result :—

	Radiation.
Oxide of cobalt . . . . .	76·5
Carbonate of zinc. . . . .	77·7

Here the black radiation is sensibly equal to the white one.

Finally, comparing black and white we have the following result :—

	Radiation.
Lampblack . . . . .	84·0
Chloride of lead . . . . .	55·4

Here the radiation from the black body far transcends that from the white one.

We have thus compared red powders with red, black with black, white with white, and black with white; and the conclusion to be drawn from the experiments is, I think, that chemical constitution, so far from being of vanishing value, is the really potent influence in the experiments.

Were the radiative power of these substances determined by the state of division, I think it must make itself sensible even in a case where the division is effected by the pestle and mortar; but I do not find this to be the case. A plate of glass was fixed against the polished surface of a Leslie's cube, and on the plate the powder of glass, rendered as fine as the pestle and mortar could make it, was strewn. It was caused to adhere without cement of any kind. The cube was filled with boiling water and presented to the thermo-electric pile until a permanent deflection was obtained. Permitting the cube to remain in its position, the powder was removed with a camel's-hair brush. An inconsiderable augmentation of the radiation was the result, the increase being such as might be expected to follow from the slight



difference of temperature between the surface of the glass plate and the powder which had been strewn upon it. Similar experiments were made with a plate of rock-salt, on which finely divided powder of rock-salt was shaken. The result was precisely similar to that obtained with the glass powder.

One side of a Leslie's cube was covered with a sheet of bright platinum-foil, and a second face by a similar sheet on which black platinum had been deposited by electrolysis. As radiators these two sheets of foil behaved in the following manner:—

	Radiation.
Bright platinum-foil . . . . .	6·0
Platinized platinum . . . . .	45·2

Here the radiation of the black platinum is nearly eight times that of the bright substance.

Having thus shown, I trust conclusively, that the influence of chemical constitution makes itself felt in all states of aggregation, for the sake of reference, I will here tabulate the results obtained with a considerable number of powders when subjected to the same conditions of experiment.

TABLE I.—Radiation from Powders imbedded in Sulphur Cement.

Substance.	Radiation.	Substance.	Radiation.
Rock-salt . . . . .	35·3	Sulphide of molybdenum.	71·3
Biniodide of mercury .	39·7	Sulphate of baryta . .	71·6
Milk of sulphur . . . .	40·6	Chromate of lead . . .	74·1
Common salt . . . . .	41·3	Red oxide of lead . . .	74·2
Yellow iodide of mercury.	46·6	Sulphide of cadmium . .	76·3
Sulphide of mercury . .	46·6	Subchloride of copper .	76·5
Iodide of lead . . . . .	47·3	Oxide of cobalt . . . .	76·7
Chloride of lead . . . .	55·4	Sulphate of lime . . . .	77·7
Chloride of cadmium . .	56·5	Carbonate of zinc . . .	77·7
Chloride of barium . . .	58·2	Red oxide of iron . . .	78·4
Chloride of silver (dark).	58·6	Sulphide of copper . . .	79·0
Fluor-spar . . . . .	68·4	Hydrated oxide of zinc .	80·4
Tersulphide of antimony.	69·4	Black oxide of iron . .	81·3
Carbonate of lime . . . .	70·2	Sulphate of iron . . . .	81·7
Oxysulphide of antimony.	70·5	Iodide of copper . . . .	82·0
Sulphide of calcium. . .	71·0	Lampblack . . . . .	84·0

I subsequently endeavoured to get rid of the sulphur cement and to make the powders adhere by wetting them with pure bisulphide of carbon, applying them to the cubes while wet. Some of the powders clung, others did not. My ingenious friend Mr. Duppa suggested to me that the powders might be held on by

electrifying the cubes. I tried this plan, and found it simple and practicable. It was, however, aided by a circumstance which we did not anticipate. The cube being placed upon an insulating stand, the powder was shaken over it, and electrified by a few turns of a machine. It was found that the cube might then be discharged and set upright, the powders clinging to it in this position. The results obtained with this arrangement are recorded in the following Table:—

TABLE II.—Radiation from Powders held by Electricity.

Substance.	Radiation.	Substance.	Radiation.
Rock-salt . . . . .	24·5	Sulphide of calcium . .	49·1
Chloride of silver (white).	25·0	Sulphate of baryta . .	51·3
Milk of sulphur . . . .	25·8	Sugar . . . . .	52·1
Biniodide of mercury . .	26·0	Red oxide of lead . .	56·5
Iodide of lead . . . . .	36·0	Sulphide of cadmium . .	56·9
Sulphide of mercury . .	30·6	Sulphate of lime . . .	59·3
Spongy platinum . . . .	31·5	Chloride of silver (black)	60·0
Washed sulphur (flowers)	32·3	Carbonate of zinc. . .	62·0
Sulphide of zinc . . . .	36·1	Oxide of cobalt . . .	62·5
Amorphous phosphorus .	38·0	Iodide of copper . . .	63·0
Chloride of lead . . . .	39·0	Red oxide of iron. . .	63·8
Chloride of cadmium. . .	40·0	Sulphide of iron . . .	65·5
Fluor-spar . . . . .	48·6	Black oxide of iron . .	65·8

The agreement as regards relative radiative power between this and the former Table is as good as could under the circumstances be expected. The experiments have been several times repeated; and the Table contains the means of the results, which were never widely different from each other.

The *quantity* of radiant heat emitted by a body in all states of aggregation having been thus conclusively shown to depend mainly upon its molecular character, the question as to the *quality* of the heat emitted next arises. In examining this point, I contented myself with testing the heat by its transmission through rock-salt. The choice of this substance involved the solution of the still disputed question whether rock-salt is equally pervious to all kinds of rays\*. For if it absorbed the radiation from two different bodies in different degrees, it would not only show a difference of quality in the radiations, but also demonstrate its own incapacity to transmit equally rays of all descriptions.

\* The last publication on this subject is from the pen of that extremely able experimenter Professor Knoblauch. After discussing the results of De la Provostaye and Desains, and of Mr. Balfour Stewart, he arrives at a different conclusion—namely, that pure rock-salt is equally pervious to all kinds of heat.—Poggendorff's *Annalen*, 1863, vol. cxx. p. 177.

The plate of rock-salt chosen for this purpose was a very perfect one. I have never seen one more pellucid. The thickness was 0·8 of an inch, and its size, compared with the aperture in front of which it was placed, was such as to prevent any part of the rays reflected from its lateral boundaries from mingling with the direct radiation. M. Knoblauch has clearly shown how the absence of caution in this particular may lead to error. The mode of experiment was that usually followed: the source was first permitted to radiate against the pile, and the deflection produced by the total radiation noted. The plate of rock-salt being then interposed, the deflection sank, and from its new value the transmission through the rock-salt was calculated and expressed in hundredths of the total radiation.

TABLE III.—Transmission through Rock-salt from the following substances raised to a temperature of 100° C.

Substance.	Transmission.	Radiation.
Rock-salt . . . . .	67·2	35·3
Biniodide of mercury . . . . .	76·3*	39·7
Milk of sulphur . . . . .	76·9*	40·6
Common salt . . . . .	70·8	41·3
Yellow iodide of mercury . . . . .	79·0*	46·6
Sulphide of mercury . . . . .	73·1	46·6
Iodide of lead . . . . .	73·8	47·3
Chloride of lead . . . . .	73·1	55·4
Chloride of cadmium . . . . .	73·2	56·5
Chloride of barium . . . . .	70·7*	58·2
Chloride of silver (dark) . . . . .	74·2	58·6
Fluor-spar . . . . .	70·5*	68·4
Tersulphide of antimony . . . . .	77·1	69·4
Carbonate of lime . . . . .	77·6	70·2
Oxysulphide of antimony . . . . .	77·6	70·5
Sulphide of molybdenum . . . . .	78·4	71·3
Sulphate of baryta . . . . .	71·3	78·4
Chromate of lead . . . . .	71·6	79·2
Red oxide of lead . . . . .	74·1	79·2
Subchloride of copper . . . . .	76·3	78·6
Oxide of cobalt . . . . .	76·5	79·7
Red oxide of iron . . . . .	78·4	81·0
Sulphide of copper . . . . .	79·0	82·3
Black oxide of iron . . . . .	81·3	82·7
Sulphide of iron . . . . .	81·7	83·3
Lampblack . . . . .	84·0	83·3

Here we have a transmission varying from 67 per cent. in the case of powdered rock-salt to 84 per cent. in the case of lamp-

black. The powders employed were fixed by the sulphur cement. The same powders held by electricity, and permitted to radiate through the rock-salt, gave the following transmissions :—

TABLE IV.

Substance.	Transmission.	Substance.	Transmission.
Rock-salt . . . .	62·8	Carbonate of zinc . .	74·8
Chloride of silver (white)	69·7	Sulphate of baryta . .	75·0
Fluor-spar . . . .	70·7	Common sugar . . .	75·4
Sulphide of mercury . .	71·0	Sulphide of copper . .	76·5
Sulphide of calcium . .	72·5	Iodide of copper . . .	76·5
Milk of sulphur . . .	72·8	Red oxide of iron . .	76·8
Sulphide of cadmium . .	73·3	Chloride of silver (black)	77·3
Biniodide of mercury . .	73·7	Amorphous phosphorus.	78·0
Washed sulphur . . .	74·0	Oxide of cobalt . . .	78·2
Iodide of lead . . . .	74·1	Sulphide of iron . . .	78·5
Sulphate of lime . . .	74·2	Black oxide of iron . .	79·7
Sulphide of zinc . . .	74·4	Black platinum . . .	89·0

The transmissions here are lower than when the sulphur cement was employed. I do not, however, think that the differences are due to the employment of the cement, but to a slight source of disturbance, which was removed in the later experiments.

For the heat emitted by black platinum rock-salt manifests its maximum power of transmission, which would lead us to ascribe a maximum dissonance between the vibrating periods of rock-salt and of black platinum. It will also be remarked that, as a general rule, the powerful radiator has its heat more copiously transmitted by the rock-salt than the feeble radiator. To render this clear, I have in Table III. appended to the transmission the corresponding total radiation. The only striking exceptions to this rule exhibited in Table III. are marked with asterisks. This result, I think, is what might fairly be expected; for the character which enables a molecule of one substance to radiate a greater quantity of heat than another, may also be expected to influence its rate of oscillation. Hence, as a general rule, a greater dissonance will exist between the vibrating periods of good radiators and bad radiators, than between the periods of the members of either class. But the greater the dissonance the less will be the absorption; hence, as regards transmission through rock-salt, we have reason to expect that powerful radiators will find a more open door to their emission than feeble ones. This is, as I have said, in general the case. But the rule is not without its exceptions; and the most striking of these is the case of black platinum, which, though but a moderate radiator,



sends a greater proportion of heat through rock-salt than any other known substance.

In his latest investigation, Knoblauch examined at great length the diathermancy of rock-salt. With his usual acuteness, he points out several possible sources of error, and with his customary skill he neutralizes these sources. His conclusion is the same as that of Melloni, namely, that rock-salt transmits in the same proportion all sorts of rays. On the opposite side we find the experiments of MM. De la Provostaye and Desains, and those of Mr. Balfour Stewart\*, both of which are discussed by Knoblauch. He differs from those experimenters, while my results bear them out. Considering the slow augmentation of transmission which the foregoing Tables reveal, and the considerable number of bodies whose heat is transmitted in almost the same proportion by rock-salt, it is easy to see that, where the number of radiants is restricted, such a uniformity of transmission might manifest itself as would lead to the conclusion of Melloni and Knoblauch. It was only by the selection and extension of the substances chosen as radiators that the differences were brought out with the distinctness recorded in the foregoing Tables.

The differences in point of quality and the absence of perfect diathermancy in rock-salt appear more striking when instead of the transmissions we take the absorptions. In the case of the radiation from powdered rock-salt, for example, 37·2 per cent. of the whole radiation is intercepted by the rock-salt plate. According to Melloni, between 7 and 8 per cent. of this is lost by reflexion at the two surfaces of the salt. This would leave in round numbers a true absorption of 30 per cent. by the plate of rock-salt. In the case of black platinum, the absorption similarly deduced amounts to only 4 per cent. of the total radiation. Instead, therefore, of the radiation from those two sources being absorbed in the same proportion, the ratio in the one case is more than seven times that in the other. For the sake of illustration here follow a few of the absorptions determined in this way:—

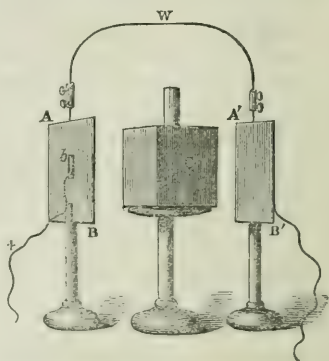
TABLE V.—Radiation through Rock-salt.

Source.	Absorption.
Black platinum . . . .	3·7
Black oxide of iron . . .	13·0
Red oxide of iron . . . .	15·9
Sugar . . . . .	17·3
Chloride of silver . . . .	22·6
Rock-salt . . . . .	29·9

\* I think the important experiment first executed by Mr. Balfour

These differences of absorption are so great as to enable every experimenter to satisfy himself with the utmost ease as to the unequal permeability of rock-salt ; and this facility of demonstration will, I trust, contribute to make inquirers unanimous on this important point.

Theory alone would lead us to the conclusion that the absorptive power of the substances mentioned in Table I. is proportional to their radiative power ; nevertheless a few actual experiments on absorption will serve as a check upon those recorded in the Table. These were conducted in the following manner :—A B is a sheet of common block tin, 5 inches high by 4 in width, fixed upon a suitable stand. At the back of A B is soldered one end of the small bar of bismuth *b*, the remainder of the bar, to its free end, being kept out of contact with the plate by a bit of cardboard. To the free end of *b* is soldered a wire which can be connected with a galvanometer. A' B' is a second plate of metal in every respect similar to A B. From



one plate to the other stretches the wire W. C is a cube containing boiling water, placed midway between the two plates of metal.

The plates were in the first instance coated uniformly with lampblack, and the two surfaces of the cube which radiated against the plates were similarly coated. The rays from C being emitted equally right and left, and absorbed equally by the two coated plates A B and A' B', warmed these plates to the same degree ; it is manifest from the arrangement that, if the thermoelectric junctions were equally sensitive, the current generated at the one ought exactly to neutralize the current from the other junction. This was found to be very nearly the case. It is difficult to make both junctions of absolutely the same sensitiveness ; but the moving of the feebler plate a hair's breadth nearer to the cube C enabled it to neutralize exactly the radiation from its opposite neighbour. My object now was to compare the lampblack coating of the plate A B with a series of other coatings, which were placed in succession on the other plate. These latter coatings were the powders already employed, and they were held upon A' B' by their own adhesion.

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Stewart, of rock-salt radiating through rock-salt, is by itself sufficient to demonstrate in the most unequivocal manner that this substance is not equally pervious to all kinds of rays.

When A B was coated with lampblack and A' B' with rock-salt powder, the equilibrium observed when both the plates were coated with lampblack did not exist. The lampblack, by its greater absorption, heated its bismuth junction most, and a permanent deflection of  $59^\circ$  in favour of the lampblack was obtained. Other powders were then substituted for the rock-salt, and the difference between them and the lampblack was determined in the same way. When, for example, sulphide of iron was employed, there was a deflection of  $30^\circ$  in favour of lampblack. The results obtained with six different powders thus compared with lampblack are given in the following Table:—

TABLE VI.

Excess of lampblack above rock-salt	. . .	$59^\circ = 112$ units.
„ „ fluor-spar	. . .	$46 = 68$ „
„ „ red lead	. . .	$40 = 45$ „
„ „ oxide of cobalt	. . .	$37 = 42$ „
„ „ sulphide of iron	. . .	$30 = 30$ „

The order of absorption here shown coincides with the order of radiation of the same substances shown in Table III. But we can go further than the mere order of absorption. Removing the opposing plate, and allowing the standard lampblack to exert its full action upon the galvanometer, the deflection observed was  $65^\circ = 163$  units.

The numbers in Table VI. show us the excess of the lampblack over the substances there employed,—its excess in the case of rock-salt, a bad absorber, being 112, its excess in the case of sulphide of iron being only 30. Deducting, therefore, the numbers given in Table VI. from 163, the total absorption of lampblack, we obtain a series of numbers which expresses the absorptions of the other substances. This series stands as follows:—

TABLE VII.

Substance.	Relative absorptions.		Radiation.
Rock-salt . . . .	51	25.5	25
Fluor-spar . . . .	95	47.5	49
Red lead . . . .	118	59.0	57
Oxide of cobalt . .	121	60.5	62
Sulphide of iron . .	133	66.5	66

The first column of figures expresses the relative absorptions; for the sake of comparison with the corresponding radiations, I have placed the halves of these numbers in the second column of figures, and in the third column the radiations obtained from

Table II. The approximation of the figures in the second and third columns is seen to be extremely close.

Throughout this investigation I have been efficiently assisted by Mr. W. F. Barrett, whose rapid progress in scientific knowledge and experimental skill during the three years that he has assisted me has given me great satisfaction.

### XXXIX. *Notices respecting New Books.*

*Memoirs of the Geological Survey of Great Britain. Vol. III.—The Geology of North Wales. By Professor A. C. RAMSAY, F.R.S., Local Director of the Geological Survey of Great Britain. With an Appendix on the Fossils; by J. W. SALTER, A.L.S., F.G.S., late Palæontologist to the Survey. London: Longmans. 8vo. 381 pp., with Maps, Sections, and 26 Plates of Fossils.*

PERHAPS no long-deferred publication has ever been looked forward to by geologists with such a continuous and well-sustained expectation as the memoir now before us. The delay in its appearance has no doubt tended to render it more complete than it would otherwise have been; and we must now recognize it as being by far the most complete exposition yet published of the Geology of North Wales.

Necessarily the memoir is chiefly descriptive, the principal design being to give "such a detailed description of the Silurian rocks of North Wales, that any one may ascertain the structure of any minor area in which he may be interested." This description occupies the bulk of the work; but it is prefaced by a general sketch of the Geology of Wales, to which we must especially draw attention.

The physical relations of the older rocks possess more general interest than the peculiarities of structure and extension of any one division; and Professor Ramsay has therefore judiciously given a brief description of them, being the result of a multitude of careful observations wherever Silurian strata occur in Britain. We thus learn that "there is no sign of unconformity anywhere between the Cambrian rocks and the overlying Lingula-flags of Merionethshire, Caernarvonshire, and the Longmynd;" but that there is probably an unconformity between the Tremadoc slates and the Lingula-flags beneath. The Llandeilo flags, which come next in the series, are also in all probability unconformable to the Tremadoc slates; for "in Anglesea strata of Llandeilo and Caradoc age lie directly on Cambrian rocks, showing so great and rapid an overlap of the Lingula and Tremadoc series, that it seems to indicate unconformity between these black slaty strata and the Tremadoc and Lingula-beds below."

The lower Llandovery strata appear to be conformable to the Bala or Caradoc beds, which are themselves conformable to the Llandeilo rocks; hence the Geological Survey have retained the lower Llandovery strata in the Lower Silurian division, while the upper



Llandovery, which are unconformable to the lower, are placed in the Upper Silurian. Professor Ramsay, indeed, states that "a great physical break takes place at this point, all the lower members of the Silurian series having been disturbed and planed across by denudation before the upper Llandovery beds were formed." The Tarannon shales are sometimes to all appearance conformable to the upper Llandovery, but sometimes distinctly overlap them; but the succeeding Wenlock and Ludlow beds are conformable to one another and to the Tarannon shales beneath. In fact it appears that there is an Upper Silurian series of conformable formations underlain by three formations unconformable to one another, namely the Tarannon shale, and the upper and lower Llandovery; and these again are underlain by a Lower Silurian series of conformable deposits. Professor Ramsay's interpretation of these facts seems very probable—namely, that the strata which "lie between the top of the Caradoc or Bala beds and the base of the Wenlock shale . . . were formed during a period of frequent oscillation of the relative level of the land to the sea. . . . Three fragments of this episode have alone been preserved; and while the oldest, that of the lower Llandovery beds, is somewhat closely connected with the Lower Silurian period, the remaining two are more nearly related to the Upper Silurian age."

Though few geologists will be inclined to oppose this view, and to give preference to that of a Middle Silurian epoch, there is another question which we think will meet with a different reception. We refer to the propriety of continuing to include the *Lingula*-flags in the Lower Silurian series. On this question, indeed, Professor Ramsay seems to accept a conclusion diametrically opposed to his own reading of the evidence, and consequently, we imagine, to his own convictions. We find him chronicling the unconformity of the overlying strata to the *Lingula*-flags, and the conformity of the latter to the Cambrians. He mentions the absence of graptolites from the *Lingula*-flags, and their occurrence in the whole of the remaining members of the Silurian system. He also quotes Mr. Salter's determinations to show the almost entire distinctness of the *Lingula*-flag, Tremadoc, and Llandeilo faunas; and he even goes so far as to say of the Cambrian deposits and the *Lingula*-flags, that, "except for the convenience of a great lithological distinction, they scarcely require separation by line and colour." All these admissions make us wonder why it should be so vehemently insisted upon that the *Lingula*-flags are Lower Silurian, not Cambrian. The only argument in its favour appears to be the "convenience" of the error. And thus our arrival at a natural classification must be postponed until "convenience" holds a lower rank than truth.

In the body of the memoir Professor Ramsay describes the Cambrian and Silurian rocks of North Wales as they occur in several typical areas; but his method is neither quite geographical nor quite stratigraphical. He has, however, succeeded in bringing out the chief features of the structure of the country, by avoiding irrelevant matters, and by giving a summary of the facts advanced, and inferences drawn, in discussing each particular area or formation.

In the Appendix, Mr. Salter gives lists of the fossils of each formation, with a few illustrative remarks on those of the older subdivisions, and descriptions of a large number of Lower Silurian and Primordial species, most of which are very well illustrated either as lithographs or engravings.

The geological portion of the Memoir is excellently illustrated by a plate of three coloured sections, one of which (No. 3) is well deserving of a careful study. There are also a geologically coloured index map of Wales, and a number of woodcut plans, sections, &c.; but the execution of the woodcuts is positively disgraceful, and appears all the worse from the excellence of the plates.

*Elements of Quaternions.* By the late Sir WILLIAM ROWAN HAMILTON, LL.D., &c. Edited by his Son, W. E. HAMILTON, B.A. London: Longmans and Co. 1866.

The method of Quaternions was first announced by the late Sir W. R. Hamilton in a communication made to the Royal Irish Academy in November 1843, in which the fundamental principles and formulæ of the method were laid down. Subsequently the subject was fully discussed and illustrated in his work entitled "Lectures on Quaternions," published in 1853. For some years previous to his death he was engaged on the present work, which is an entirely new exposition of the method. It is indeed (to use the author's own words) "founded on the same principles as the lectures, but the plan adopted is entirely new; and the present work can in no sense be considered as a second edition of that former one."

The arrangement of the work is as follows:—The first Book treats of vectors, without reference to angles or rotations. The second Book treats of quaternions considered as quotients of vectors. The third Book treats of quaternions considered as products or powers of vectors. The object of this arrangement is to develop the method from its simpler to its most general form. It would, of course, have been possible to have begun with the general principles of the subject, and to have treated the less general parts as particular cases; and each way would have had its own advantages. In the case, however, of a subject like quaternions, which might, without much inaccuracy, be described as a particular kind of algebra, the rules and symbols of which resemble, but are not identical in meaning with, those of ordinary algebra, it is, of course, a great gain for the student to see the method built up from its first principles, and to observe the way in which the necessity arises for interpreting symbols and expressions in the particular mode required by the method.

It is to be observed that the work was designed by Sir W. Hamilton for the use of students; and, apparently for the purpose of carrying out this design, he drew up a most elaborate table of contents to the work. This Table occupies fifty-seven pages, and embraces a sort of running comment on the leading portions of the work, in some cases directing the reader's special attention to certain articles, in others recommending the omission of certain parts on the first perusal, in others explaining the relation in which the contents of one or more articles

stand to the general plan of the work, &c. We are inclined to infer, from the author's evident anxiety to assist the student, that he had not been altogether satisfied with the progress hitherto made by the method of quaternions towards general use, and that he imputed this to the difficulties to be encountered at the beginning of the subject. Every part of the subject is profusely illustrated by applications, showing, if any doubt existed on that head, the fertility of the method, and its applicability to every branch of mathematical science. Without attempting to enumerate these applications, but merely to give a notion of the varied contents of the work, we may mention that in the first book the method of vectors is applied to geometrical nets both plane and in space, to barycentres of systems of points, to anharmonic equations of curves and surfaces, &c., and that, besides other illustrations interspersed through the work, the last chapter, comprising near upon three hundred closely printed pages, is entirely taken up by applications of the method. These are, in the first place, to purely geometrical questions—to tangents and to normal and osculating planes of curves in space, to geodetic lines, to involutes and evolutes in space, &c.; in the second place, to physical questions—amongst others, to the dynamics of a rigid body, to that of a system of mutually attracting points, to the undulatory theory of light, &c.

With the commencement of an article "On MacCullagh's Theorem of the Polar Plane" the work abruptly terminates. The author was engaged on the work at the time of his death, and the editor rightly considered that his duty both to the author and the public would be most fully discharged by simply giving to the world what had been written. "I came to the conclusion," he says, "that my duty was to publish the work as I found it, adding merely proof-sheets partially corrected by my late father, and from which I removed a few typographical errors, and editing only in the literal sense of giving forth."

The work, though unfinished, will remain a monument both of the subtlety and originality of Sir W. Hamilton's mind, and of his profound and extensive knowledge of every branch of mathematical science. Whether the method he originated will ever be largely used by other mathematicians remains to be seen; but that it is a calculus of enormous power and of indefinitely extensive application cannot be doubted. Indeed, in addition to the applications contained in the work, several others had been contemplated by Sir W. Hamilton, though he well knew that he would be unable to exhaust them. We learn this from the editor's statement:—"Shortly before my father's death I had several conversations with him on the subject of the 'ELEMENTS.' In these he spoke of anticipated applications of quaternions to electricity, and to all questions in which the idea of polarity is involved—applications which he never in his own lifetime expected to be able fully to develope."



XL. *Proceedings of Learned Societies.*

## ROYAL SOCIETY.

[Continued from p. 230.]

May 17, 1866.—Lieut.-General Sabine, President, in the Chair.

THE following communication was read:—

“On the Spectrum of a New Star in Corona Borealis”\*. By William Huggins, F.R.S., and W. A. Miller, M.D., Treas. R.S.

Yesterday, May the 16th, one of us received a note from Mr. John Birmingham of Tuam, stating that he had observed on the night of May 12 a new star in the constellation of Corona Borealis. He describes the star as “very brilliant, of about the 2nd magnitude.” Also Mr. Baxendell of Manchester wrote to one of us giving the observations which follow of the new star, as seen by him on the night of the 15th instant.

“A new star has suddenly burst forth in Corona. It is somewhat less than a degree distant from  $\epsilon$  of that constellation in a southeasterly direction, and last night was fully equal in brilliancy to  $\beta$  Serpentis or  $\nu$  Herculis, both stars of about the 3rd magnitude.”

Last night, May 16, we observed this remarkable object. The star appeared to us considerably below the 3rd magnitude, but brighter than  $\epsilon$  Coronæ. In the telescope it was surrounded with a faint nebulous haze, extending to a considerable distance, and gradually fading away at the boundary†. A comparative examination of neighbouring stars showed that this nebulosity really existed about the star. When the spectroscope was placed on the telescope, the light of this new star formed a spectrum unlike that of any celestial body which we have hitherto examined. The light of the star is compound, and has emanated from two different sources. Each light forms its own spectrum. In the instrument these spectra appear superposed. The principal spectrum is analogous to that of the sun, and is evidently formed by the light of an incandescent solid or liquid photosphere, which has suffered absorption by the vapours of an envelope cooler than itself. The second spectrum consists of

\* The Astronomer Royal wrote to one of us on the 18th, “Last night we got a meridian observation of it; on a rough reduction its elements are—

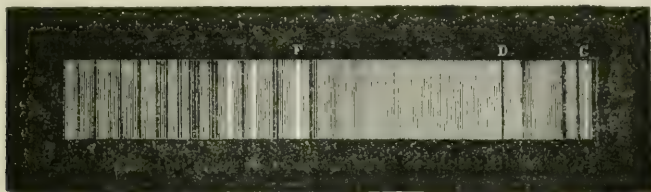
R.A. 1866, May 17.....	15 <sup>h</sup> 53 <sup>m</sup> 56 <sup>s</sup> .08,
N.P.D.....	63° 41' 53",

agreeing precisely with Argelander, No. 2765 of ‘Bonner Sternverzeichniss,’ declination  $+26^{\circ}$ , magnitude 9.5.” Mr. Baxendell writes on the 21st, “It is probable that this star will turn out to be a variable of long or irregular period, and it may be conveniently at once designated  $\tau$  Coronæ.” Sir John Herschel informs one of us that on June 9, 1842, he saw a star of the 6th magnitude in Corona very nearly in the place of this strange star. As Sir John Herschel’s position was laid down merely by naked-eye allineations, the star seen by him may have possibly been a former temporary outburst of light in this remarkable object.

† On the 17th this nebulosity was suspected only; on the 19th and 21st it was not seen.



a few bright lines, which indicate that the light by which it is formed was emitted by matter in the state of luminous gas\*. These spectra are represented with considerable approximative accuracy in a diagram which accompanies this paper.



Spectrum of Absorption and Spectrum of Bright Lines forming the Compound Spectrum of a New Star near  $\epsilon$  Coronæ Borealis.

*Description of the spectrum of absorption.*—In the red a little more refrangible than Fraunhofer's C are two strong dark lines. The interval between these and a line a little less refrangible than D is shaded by a number of fine lines very near each other. A less strongly marked line is seen about the place of solar D. Between D and a portion of the spectrum about the place of  $b$  of the solar spectrum, the lines of absorption are numerous, but very thin and faint. A little beyond  $b$  commences a series of close groups of strong lines; these follow each other at small intervals, as far as the spectrum can be traced.

*Description of the gaseous spectrum.*—A bright line, much more brilliant than the part of the continuous spectrum upon which it falls, occupies a position which several measures make to be coincident with Fraunhofer's F†. At rather more than one-fourth of the distance which separates F from G, a second and less brilliant line was seen. Both these lines were narrow and sharply defined. Beyond these lines, and at a distance a little more than one-third of that which separates the second bright line from the strongest bright one, a third bright line was observed. The appearance of this line suggested that it was either double or undefined at the

\* The position of the groups of dark lines shows that the light of the photosphere, after passing through the absorbent atmosphere, is yellow. The light, however, of the green and blue bright lines makes up to some extent for the green and blue rays (of other refrangibilities) which have been stopped by absorption. To the eye, therefore, the star appears nearly white. However, as the star flickers, there may be noticed an occasional preponderance of yellow or blue. Mr. Baxendell, without knowing the results of prismatic analysis, describes the impression he received to be "as if the yellow of the star were seen through an overlying film of a blue tint."

† On the 17th, the lines of hydrogen, produced by taking the induction-spark through the vapour of water, were compared in the instrument simultaneously with the bright lines of the star. The brightest line coincided with the middle of the expanded line of hydrogen which corresponds to Fraunhofer's F. On account of the faintness of the red end of the spectrum, when the amount of dispersion necessary for these observations was employed, the exact coincidence of the line in this part of the spectrum with the red line of hydrogen, though extremely probable, was not determined with equal certainty.

edges. In the more refrangible part of the spectrum, probably not far from G of the solar spectrum, glimpses were obtained of a fourth and faint bright line. At the extreme end of the visible part of the less refrangible end of the spectrum, about C, appeared a line brighter than the normal relative brilliancy of this part of the spectrum. The brightness of this line, however, was not nearly so marked in proportion to that of the part of the spectrum where it occurs, as was that of the lines in the green and blue\*.

*General Conclusions.*—It is difficult to imagine the present physical constitution of this remarkable object. There must be a photosphere of matter in the solid or liquid state emitting light of all refrangibilities. Surrounding this must exist also an atmosphere of cooler vapours, which give rise by absorption to the groups of dark lines.

Besides this constitution, which it possesses in common with the sun and the stars, there must exist the source of the gaseous spectrum. That this is not produced by the faint nebosity seen about the star is evident by the brightness of the lines, and the circumstance that they do not extend in the instrument beyond the boundaries of the continuous spectrum. The gaseous mass from which this light emanates must be at a much higher temperature than the photosphere of the star; otherwise it would appear impossible to explain the great brilliancy of the lines compared with the corresponding parts of the continuous spectrum of the photosphere. The position of two of the bright lines suggests that this gas may consist chiefly of hydrogen.

If, however, hydrogen be really the source of some of the bright lines, the conditions under which the gas emits the light must be different from those to which it has been submitted in terrestrial observations; for it is well known that the line of hydrogen in the green is always fainter and more expanded than the brilliant red line which characterizes the spectrum of this gas. On the other hand, the strong absorption indicated by the line F of the solar spectrum, and the still stronger corresponding lines in some stars, would indicate that under suitable conditions hydrogen may emit a strong luminous radiation of this refrangibility†.

The character of the spectrum of this star, taken together with its sudden outburst in brilliancy and its rapid decline in brightness, suggest to us the rather bold speculation that, in consequence of some

\* The spectra of the star were observed again on the 17th, the 19th, the 21st, and the 23rd. On these evenings no important alteration had taken place. On the 17th and succeeding evenings, though the spectrum of the waning star was fainter than on the 16th, the red bright line appeared a little brighter relatively to the green and blue bright lines. On the 19th and 21st the absorption lines about *b* were stronger than on the 16th. From the 16th the continuous spectrum diminished in brightness more rapidly than the gaseous spectrum, so that on the 23rd, though the spectrum as a whole was faint, the bright lines were brilliant when compared with the continuous spectrum.

† On the dependence of the relative characters of the bright lines of hydrogen upon conditions of pressure and temperature see Plücker and Hittorf, *Phil. Trans.* 1855, p. 21

vast convulsion taking place in this object, large quantities of gas have been evolved from it, that the hydrogen present is burning by combination with some other element and furnishes the light represented by the bright lines, also that the flaming gas has heated to vivid incandescence the solid matter of the photosphere. As the hydrogen becomes exhausted, all the phenomena diminish in intensity, and the star rapidly wanes.

In connexion with this star, the observations which we made upon the spectra of  $\alpha$  Orionis and  $\beta$  Pegasi, that they contain no absorption lines of hydrogen, appear to have some new interest. The spectra of these stars agree in their general characters with the absorption spectrum of the new star. The whole class of white stars are distinguished by having hydrogen lines of extraordinary force. It may also be mentioned here that we have found that the spectra of several of the more remarkable of the variable stars, namely those distinguished by an orange or ruddy tint, possess a close general accordance with those of  $\alpha$  Orionis,  $\beta$  Pegasi, and the absorption spectrum of the remarkable object described in this paper. The purely speculative idea presents itself from these observations, that hydrogen probably plays an important part in the differences of physical constitution which apparently separate the stars into groups, and possibly also in the changes by which these differences may be brought about\*.

## *XLI. Intelligence and Miscellaneous Articles.*

ON THE FIGURE OF THE EARTH MEASURED GEODETICALLY.

BY ARCHDEACON PRATT, M.A., F.R.S.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

Near Alexandria,  
September 10, 1866.

WITH reference to Captain Clarke's letter to you, which appears in your Magazine for this month (September), and my paper in your July Number, I beg to say that, through inadvertence, or, in plain English, a blunder, I wrote down the wrong formula for my

\* Mr. Baxendell sends us the following Table of magnitudes:—

	<sup>h</sup>	<sup>m</sup>			
May 15 at 12	0	G.M.T.,	$\tau$ Coronæ	= 3·6 or 3·7	magnitude.
„ 16 „ 10	30	„	„	= 4·2	
„ 17 „ 11	0	„	„	= 4·9	
„ 18 „ 12	30	„	„	= 5·3	
„ 19 „ 12	15	„	„	= 5·7	
„ 20 „ 12	30	„	„	= 6·2	
„ 21 „ 12	0	„	„	= 7·3	
„ 22 „ 11	15	„	„	= 7·7	
„ 23 „ 10	30	„	„	= 7·9	
„ 24 „ 10	30	„	„	= 8·1	



correction  $z$ . Instead of

$$z = - \frac{(m) + (\alpha)U + (\beta)V}{i},$$

I ought to have written as follows :

$$z = - \frac{(m) + (\alpha)U + (\beta)V}{i} + \frac{(t)}{i} - t,$$

a constant quantity as before.

This alteration will make the following changes in paragraph 6 of my paper in your July Number. To  $z_1, z_2, z_3$  must be added

$$\frac{(t_1)}{i} - t_1, \quad \frac{(t_2)}{i} - t_2, \quad \frac{(t_3)}{i} - t_3.$$

This will lead to the following results :—

$$\frac{(t_1)}{i} = -0''\cdot05, \quad \frac{(t_2)}{i} = 0''\cdot54, \quad \frac{(t_3)}{i} = -0''\cdot05.$$

These angles, therefore,  $-0''\cdot05, 0''\cdot54, -0''\cdot05$ , are not the local-attraction-deflections at the *reference-stations* of the Anglo-Gallic, Russian, and Indian arcs, but are the *averages* of the deflections caused by local attraction at *all* the stations of the several arcs.

2. I will not occupy your pages by showing how I come to this result, as I purpose taking up this very important subject elsewhere, and more at length than your space will allow. I will merely add that it will appear that in every case the unknown quantity which enters into the formulæ for the axes of the earth, derived from the measurement of any arc, when local attraction is taken account of, is the average local deflection of all the stations of the arc, and not the deflection at the reference-station merely. It may appear from this that my revised method for using the principle of least squares introduces several unknown quantities instead of one, viz. the local deflections at all the stations of the arc instead of at the reference-station only. But as the difference of local deflection at any two stations on the arc is exactly measured by the difference between the astronomical and geodetical amplitudes of the stations, one of which is known by observation, and the second by calculation, the average of all the local deflections can always be expressed in terms of the deflection at the reference-station, or at any other single station of the arc.

3. The calculation of the semiaxes in my paper in No. 64 of the Royal Society's 'Proceedings' remains as before, and makes them

20,926,189 and 20,855,316 feet.

4. As  $-0''\cdot05, 0''\cdot54, -0''\cdot05$  are now the average local deflections of the whole arc and not merely of the reference-station, the actual local deflections at the several stations will have to be re-determined.

5. The data for doing this for the Indian arc I have at hand (see my 'Figure of the Earth,' 3rd edit. p. 148). Let  $t, t', t'', t'''$  be the



local deflections at Punno, Damargida, Kalianpur, and Kaliana. Then

$$t'-t=-1''\cdot50, \quad t''-t'=+3\cdot61, \quad t'''-t''=-4''\cdot20.$$

But by the last paragraph,

$$\frac{t+t'+t''+t'''}{4}=-0''\cdot05.$$

These four equations give

$$t=0''\cdot32, \quad t'=-1''\cdot18, \quad t''=2''\cdot43, \quad t'''=-1''\cdot77$$

for the local deflections at the four stations of the great arc from Cape Comorin to the Himalayas. They are very small quantities compared with the local deflections which calculation gives for the combined effect of the Himalayas and the ocean (Figure of the Earth, p. 149), viz.

$$+22''\cdot21, \quad +17''\cdot23, \quad +21''\cdot05, \quad 34''\cdot16.$$

This shows that the variations of density in the crust below must very nearly compensate for the effect of the visible causes existing in the mountains and ocean. It follows that the concluding section of my paper in No. 64 of the Royal Society's 'Proceedings,' regarding the constitution of the earth's crust, remains unaffected by the revise of my method of applying the principle of least squares.

I am, yours faithfully,

JOHN H. PRATT.

#### ON THE SPECTRUM OF AQUEOUS VAPOUR. BY M. JANSSEN.

I have the honour to communicate to the Academy the discovery of a new optical property of aqueous vapour, a property which would appear to lead to important results in celestial physics and in meteorology. The optical study of this vapour shows that it possesses an elective power of absorption for light, or, in other words, that this vapour produces dark lines and bands in the spectrum of a luminous ray which traverses a sufficient thickness of it. But before entering into the detail of my observations, I shall request permission to give an abridged account of the researches which have led to the present investigation.

We know that the illustrious Brewster discovered in 1833 what we call atmospheric or telluric rays of the solar spectrum. Brewster had observed that when the sun was near the horizon, its prismatic image became enriched by new dark bands. This fact, in connexion with others of the same kind—that is to say, the action of nitrous gas and others which produce dark bands in the spectrum of a luminous beam which has traversed them—had led the English physicist to the extremely correct idea that our atmosphere might act like nitrous gas, and thus give rise to the dark bands observed when the sun is in the horizon; Brewster even had the idea that all the lines of the solar spectrum might be explained in the same manner. This beautiful conception could not be demonstrated completely. In

fact these dark lines generally disappeared when the sun rose, and there were no appreciable traces when the sun passed the meridian.

Subsequently, a direct experiment, in which Messrs. Brewster and Gladstone endeavoured to reproduce the gaps in the solar spectrum by analyzing at a great distance an artificial light with a continuous spectrum, did not give a satisfactory result (*Philosophical Transactions*, 1860).

The question of the origin of the dark lines and bands of the solar spectrum was not then resolved; but Brewster's beautiful researches had nevertheless introduced into science very important ideas, and facts which were to serve as the basis of ulterior studies.

A short time after the publication of the important memoir of Messrs. Brewster and Gladstone, a memoir which epitomizes the labours of these gentlemen on this question, M. Kirchhoff published his beautiful investigations on the solar spectrum. The result of these investigations is well known. The origin of spectral lines was referred to an atmosphere surrounding the sun; and the investigation of these lines revealed the chemical composition of this atmosphere. The general results of this theory will be a permanent acquisition to science; but the object was even exceeded. Between Brewster's ideas seeking to explain the solar spectrum by the action of the earth's atmosphere, and those of M. Kirchhoff assigning its origin to a solar atmosphere, there was place for a doctrine less exclusive and more complete, which will take into account the two causes, and demonstrate the twofold origin of the lines which Wollaston and Fraunhofer had discovered in the prismatic image of the sun.

The solar origin of a portion of the lines of the spectrum of this star being demonstrated, the action of our atmosphere remained to be proved by completing the researches of Messrs. Brewster and Gladstone, Piazzi Smyth, &c. That is the object of the investigations I have been engaged on since 1862.

By new optical arrangements I first established the fact that Brewster's bands were formed of a number of fine lines resembling the solar lines properly so called. Further, the study of these lines has shown that they were constant in the spectrum, although incessantly variable in their intensity with the height of the sun, that is to say, with the thickness of our atmosphere traversed by the lines of this star. These results demonstrated the action of our atmosphere. To corroborate them, I have investigated the spectrum on a high mountain (the Faulhorn), September 1864. There I observed that the lines of terrestrial origin grew weaker in proportion as I ascended—that is, in proportion as the solar lines traversed a smaller thickness of the terrestrial atmosphere. Lastly, in an experiment made on the Lake of Geneva (October 1864), I was able artificially to reproduce the same lines. The flame of a large log of spruce-fir, which gives scarcely any line but the brilliant one of sodium, exhibited, at a distance of 21 kilometres, the atmospheric lines of the solar spectrum. This accumulation of proofs showed, then, obviously the action of our atmosphere, and the twofold origin of the lines of the solar spectrum. I may add that this atmosphere, in spite of its small height and the

low temperature of the gases which form it, acts on light as energetically as, though in a different manner from the sun's atmosphere. The earth's atmosphere produces in the red, orange, and yellow of the spectrum a system of lines ten times as numerous as the solar lines of these regions. On the contrary, in the green, the blue, and the violet, the lines of solar origin predominate. Thus these two atmospheres, so different in their own temperatures, are not less so in their actions upon light. In a certain sense they divide the spectrum: the atmosphere of the earth, an atmosphere at a low temperature, acts specifically on the rays of great wave-length; the solar atmosphere, an atmosphere with a high temperature, exerts its relative action upon rays of short wave-length. This subject will have to be reverted to.

The action of our atmosphere being demonstrated, it remained to inquire to what elements of this atmosphere this action must be attributed.

An attentive study of the solar spectrum had led me, a couple of years ago, to attribute to the aqueous vapour dissolved in our atmosphere a very important, if not an entire part in the production of the telluric lines of the solar spectrum\*.

In fact, comparisons, followed for a long time, on the solar light during various seasons of the year showed very clearly that for the same heights of the sun certain lines of the spectrum of this star were more pronounced as the dew-point was higher.

Observations which I have made on the Faulhorn further confirm this view; for on extremely dry days I have seen the lines in question disappear almost entirely from the spectrum.

Thus, in the experiment on the Lake of Geneva, I have been led to choose this place as the basis of experiments by the consideration that the luminous pencil, in grazing the surface of the water, must traverse layers of air which are necessarily more moist, which would add to the chances of success; and the result has confirmed this notion.

There could thus be little doubt as to the action of aqueous vapour; yet it was necessary, seeing the importance of the result, to submit this point of theory to a direct verification, by investigating the modifications which a well-defined beam of light of known composition experienced by the fact of its passage through a tube of sufficient length containing only aqueous vapour.

This experiment presented, unfortunately, great practical difficulties. Our atmosphere contains such a quantity of aqueous vapour, that to realize artificially the effects it produced on solar light, I was led to the use of apparatus of exaggerated dimensions and difficult to manipulate.

A first trial was made at the central workshop for lighthouses†. M. Allard, chief engineer at this establishment, was so good as to

\* See, in reference to this, the discussion which has arisen between Father Secchi and myself, *Comptes Rendus*, July 12, 1863; July 27, 1863; July 25, 1864; January 30, 1865.

† *Comptes Rendus*, January 30, 1865.



lend me his help; but the tube of 10 metres which we put up for this purpose was not long enough to exhibit the phenomena sufficiently.

I was ultimately able to realize more favourable conditions. A friend of mine, M. Goschler, director of studies at the central School of Architecture, introduced me to the director of the Paris Gas Company, and to M. Arson, chief engineer. These gentlemen placed at my disposal, with a kindness for which I am greatly obliged, the ample resources of this vast establishment.

An iron tube 37 metres in length was mounted; it was placed in a wooden box of the same length, filled with well-dried wooden shavings, an arrangement which avoids all appreciable loss of heat. The vapour was furnished by a moveable steam-engine of six-horse power, and the light by a lamp of six jets placed in the direction of the axis of the tube. This light, which, as we know, gives a continuous spectrum, enables us to perceive the production of the feeblest dark bands.

These experiments are now being continued, and I wish simply to communicate to the Academy the first results. These results confirm already, in the completest manner, what the study of the solar spectrum had already indicated.

In one experiment (August 3, 1866), in which the tube, well freed from air, was full of vapour at the pressure of seven atmospheres, the spectrum was observed with five dark bands, two of which, well marked, spread from D to A (Fraunhofer), and recalled the solar spectrum seen in the same instrument towards sunset.

From the first comparisons made between the spectrum of aqueous vapour and that of solar light, the group A of Fraunhofer, B (in great part at least), the group C, and two groups between C and D are due to the action of the aqueous vapour of the atmosphere.

This experiment has further given an interesting result. The spectrum of the transmitted light was seen to be very dark in the most refrangible part, while it was brilliant in the regions of red and of yellow. Thus, although aqueous vapour energetically absorbs certain red and yellow rays, it is very transparent for most of these rays, while it acts in a general manner on the more refrangible rays. It follows from this that aqueous vapour would be of an orange-red colour by transmission, and the redder the greater the thickness through which it acts.

This result will have to be verified and established with the greatest care, and I only offer it with reserve. If it be finally demonstrated, we shall find in it an explanation of the red colour, so variable in its tints, but always observed at sunset as well as at sunrise.

The consequences of this discovery of the spectrum of aqueous vapour will be overlooked by no one. We are finally agreed as to the origin of a considerable portion of the rays of the solar spectrum; and the knowledge of these rays will allow us to investigate the higher regions of our atmosphere as regards their humidity, regions which at present are inaccessible to our means of investigation. But it is more especially in astronomy that the results will be interesting



to develop. Relying on the exact knowledge of this spectrum of aqueous vapour, I calculate on soon being in a position to pronounce on the presence of this principal element of organic life in the atmospheres of the planets and other stars. I can at once announce that this vapour forms no part of the solar atmosphere.—*Comptes Rendus*, August 13, 1866.

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ON THE PRODUCTION OF OZONE. BY M. G. PLANTÉ.

The inoxidizable metals, such as gold and platinum, have hitherto been regarded as those which alone can be used as electrodes in obtaining ozone by the electrolytic decomposition of water. I have, however, found that ozone can be obtained as well by electrodes of lead as by electrodes of platinum, and even in greater quantity.

This can be readily established by taking two voltameters, one with platinum wires, the other with lead wires of the same length and diameter, and passing the same current through them. By suspending iodized starch-paper in open tubes placed over the positive wire of each voltameter, both are at once seen to become blue, but that placed over the lead wire more rapidly and with greater intensity than that over the platinum wire.

When ozonized oxygen is simultaneously disengaged in similar solutions of iodide of potassium, the solution in which is the lead wire becomes yellow more rapidly than that in which is the platinum; and taking the quantity of iodine liberated in the latter as unity, that furnished by the ozone of the voltameter with lead wires is approximately equal to 1.5. In other words, the quantity of ozone from the platinum is only two-thirds of that from the lead.

In the smell also, and in the rapidity of the oxidation of silver, there is also an appreciable difference.

This greater abundance in the production of ozone from electrodes of lead than from electrodes of platinum is a difficult fact to explain in the present state of our knowledge of ozone. When ozone is produced by statical or induced electricity, the nature of the electrodes between which the spark passes has no appreciable influence. But when prepared by means of the pile, the nature of the electrodes exerts a preponderating influence. In the present case a metal more oxidizable than platinum produces the ozone. The oxidation, it is true, is merely superficial; the thickness of the layer does not appreciably increase as the current continues, and the volume of oxygen is not diminished as compared with that produced by platinum under the same conditions. Yet this layer of oxygen serves a double purpose; it is the source of a secondary energetic current, and at the same time it facilitates the production of ozone.

To account for the manner in which it acts in the latter case, we can only make hypotheses, useless now to dwell upon. I shall limit myself to saying that at present, to prepare ozone by the electrolysis of water, wires of lead must be used instead of those of platinum.—*Comptes Rendus*, July 23, 1866.

## ON THE DIFFUSION OF GASES THROUGH CAOUTCHOUC.

BY ARONSTEIN AND SIRKS.

Prof. Ryhe needed one day for a physical experiment a long continuous current of pure hydrogen gas. He noticed that, in spite of all precautions, it always contained traces of oxygen, nitrogen, and aqueous vapour. The connexions between the various apparatus for drying and purifying were effected by means of caoutchouc tubes. Hence he imagined the origin of the impurity must be sought in a diffusion of the gases through the caoutchouc. As the statements regarding the permeability of gases through caoutchouc are antiquated and discordant, we investigated the matter, with the following results.

In one neck of a flask filled with hydrogen a manometer-tube was fitted air-tight; the other neck, by means of a glass tube fitting air-tight, was placed in connexion with a caoutchouc tube, which was closed by a sealed glass tube. The height of the manometer was so regulated that the pressure for the same volume of gas in the flask could be read off. The diminution of the volume in the flask is then calculated by the formula

$$\delta = 1 - \frac{H'(1 + \alpha t)}{H(1 + \alpha t')},$$

where  $H$  and  $t$  denote the pressure and temperature at the beginning,  $H'$  and  $t'$  pressure and temperature at the end of the observation, and  $\alpha$  the coefficient of cubical expansion of hydrogen. The quantity of hydrogen which has passed out, and of air which has entered, may then be approximately calculated by Graham's law.

1. An ordinary vulcanized caoutchouc tube, of 3360 square millims. surface and 1.2 millim. thickness, gave in three days  $\delta = 0.0405$ . This corresponds approximately to  $5\frac{1}{2}$  per cent. of hydrogen which has passed out, and  $1\frac{1}{2}$  per cent. of air which has entered.

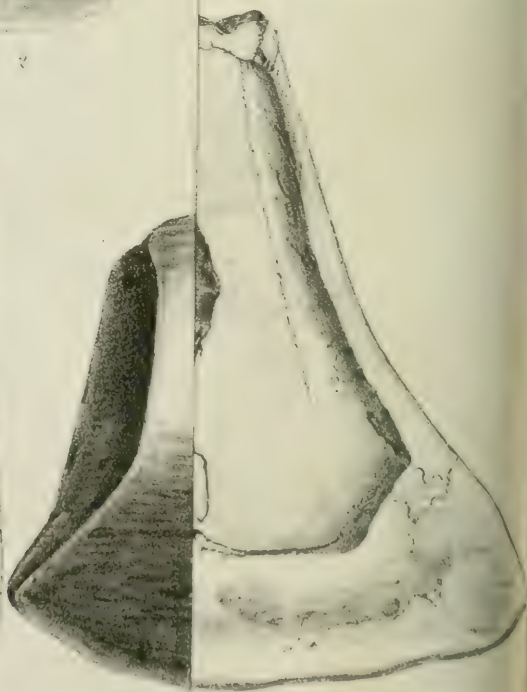
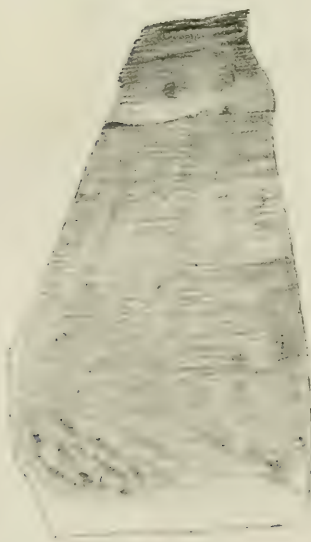
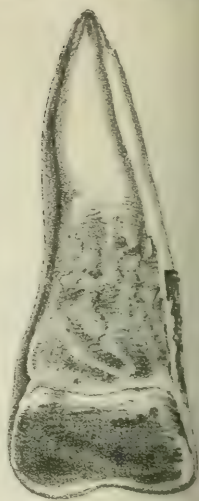
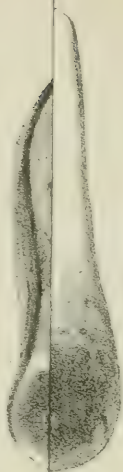
2. A brown caoutchouc tube, of the kind called devulcanized, having a surface of 3400 square millims. and a thickness of 1.6 millim., gave in twelve days  $\delta = 0.049$ , which corresponds to 6.6 per cent. of diffused hydrogen, and 1.7 per cent. infused air.

3. A tube made of unvulcanized caoutchouc, of about 5000 square millims. surface and 1.3 millim. thickness, gave in twenty-eight days  $\delta = 0.168$ , corresponding to 22.7 per cent. of diffused hydrogen, and 5.9 per cent. infused air.

Caoutchouc may be made impermeable to gases by a coating of asphalté dissolved in tar. The tubes thus coated gave, even after long standing,  $\delta = 0$ . Between caoutchouc and glass there is no diffusion, as was shown in a tube which was firmly bound to glass, and then coated with asphalté and tar, where it was not in contact with glass.—*Zeitschrift für Chemie*, May 15, 1866.

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XLII. *On Ancient Shell Mounds at St. Andrews.*—Part I.  
By ROBERT WALKER\*.

[With a Plate.]

SHELL-mounds, since attention was first directed to them by the discoveries of the Danish archæologists, have been found on several parts of the coast of Scotland; and it would appear that similar mounds have been also observed on the coast of England. Previously to the discovery of shell-mounds, nearly all the knowledge we possessed of the customs of the prehistoric inhabitants of this and other countries had been mainly derived from their tumuli, cairns, cists, &c. In some of these ancient monuments we find a group of large cinerary urns containing calcined bones only, or weapons and ornaments laid by the remains of the deceased. Sometimes the small rudely made clay urn is empty, occasionally containing fragments of bone; scattered about are the remains of the funeral feast, and in some cases the relics of the human victims that had been sacrificed to the manes of the dead. In these we recognize the sepulchral customs that characterized the different epochs, and which were perhaps gradually changed from time to time, in accordance with the different phases of civilization and their modifying influence on the savage creed. Whether, however, we regard the different kinds of tumuli and their contents as the remains of the same race, whose ideas on the subject had undergone a change, or consider them an evidence of a change of the races themselves, as indeed seems borne out by the crania, they are valuable enough;

\* Communicated by the Author, having been read before the Literary and Philosophical Society of St. Andrews.

but as to the social condition and everyday life, so to speak, of the people who practised these rites they tell us little or nothing. In the shell-mounds, on the other hand, and more especially in the lake-dwellings, we can see, to some extent at least, the social condition attained by the people. The animals which they had captured or domesticated, the plants they cultivated, their mode of treating the bones in order to extract the marrow and animal juice, their culinary vessels, their domestic and war-like implements, are all brought to light. Last, though not least, we are in this way made acquainted with the animals and plants that were the contemporaries of primeval man, and how far he was then able to subordinate them to his wants at a remote period of his existence, in the investigation of which written history lends us no aid. The mound with which we are more immediately concerned was discovered in the summer of 1864, during the cutting of a main drain along the scores on the north side of St. Andrews. The mound, at the place where the drain passes through it, is about 55 yards from the edge of the cliff, which presents a perpendicular face to the sea of about 45 feet in height. The sea washes against the bottom of it at half tides. This kitchen heap lay at a depth of 3 feet from the surface; its greatest thickness was 18 inches; its length, so far as exposed, about 70 yards; and it was laid on a stratum of drift, sand, and gravel, which had evidently been the surface of the ground previously to the accumulation of the shell-mound. The superincumbent mass was chiefly black earth. The contents of the mound consisted of shells, broken bones, fragments of pottery, and two or three stone weapons. No metallic implement or ornament of any kind was turned up, so far as I could learn. About the same time some workmen, in digging the foundation of two houses about halfway between the thickest part of the deposit and the sea, cut through what appeared to be the thin edge of the bed, and dug up a great number of fragments of pottery, pieces of bones (some of them burnt), shells, and a considerable number of broken and chipped stones; amongst them there were a few better-shaped articles, which had evidently been intended for weapons. All these things lay from 2 to 3 feet from the surface, and were somewhat mixed with the upper part of the drift bed, which appeared to have been a good deal disturbed at some former period. This appeared to me, from the marks of fires at two or three places (and some of them were pretty distinct), to be the place where the ancient mound-builders had had their dwellings. Whether the fires were kept outside or inside may not be easy to say; at all events, at one place at least the fire had undoubtedly been kindled in a hole dug in the ground perhaps a foot or more in depth; the surrounding

stones and gravel were cracked and run together by the heat, and of a somewhat darker colour than the rest of the bed: when struck by the workmen's tools it rose in concrete masses. The shells most abundant at both places, more especially at the former, were the Mussel (*Mytilus edulis*), the Cockle (*Cardium edule*), two species of Periwinkle (*Littorina littorea* and *littoralis*), and the Limpet (*Patella vulgata*). Besides these, there were a few specimens of *Nassa reticulata*, *Buccinum undatum*, *Venus striatula*, and *Venus casina*. The *Buccina* were in general broken; and from the numerous fragments of the periwinkles, it would appear that a similar mode of treatment had been frequently applied to that shell. This may have been considered the most expeditious way of getting at the contents. The mussels were very friable, and often went to pieces on being raised; the rest of the bivalves were in good order. The mammalian bones comprise two species of the Ox, the Horse, Pig, Sheep, Goat, Dog, Fox, Cat, and the Deer. There were two or three pieces of the limb-bones of birds. Of the bones of fishes, although I diligently searched for them, I could find only two centra of vertebræ. Of the bones of these animals, those of the small Ox (*Bos longifrons*) were by far the most abundant; and although the bones of the large Ox, which from the horn-cores I take to be *Bos frontosus*, were not nearly so numerous as those of its smaller congener, still, so far as they go, it was mainly the same parts that have been preserved of both. These consist of the horn-cores, some of them broken off at the base; others have part of the bones of the skull attached, and look as if the cranium had been rudely torn asunder. In one instance the horn-cores of the small Ox are held together by the intervening part of the skull, which has been broken away in front and behind to nearly a line with their base. There were also parts of the upper and lower jaws, chiefly of the small Ox, some of them containing the teeth *in situ*. The only other portions of the cranium preserved were one or two fragments of the bony ring that surround the eye. The vertebræ had likewise disappeared, with the exception of one or two of the cervicals. Of the limb-bones there were pieces of the tibia, the radius, and ulna, the metacarpus, metatarsus, os calcis, astragalus, and some of the phalanges, including the os pedis. There were only one or two pieces of the humerus, and one or two pieces of the femur; in both it was the lower joint. Moreover, although the distal end of the tibia was common enough, the proximal end seemed to be altogether absent. The scarcity of the upper bones of the limbs, compared with the numerous fragments of the lower, was not a little curious, more especially when we bear in mind that, in this respect at least, the mound in question corresponds closely with Danish kitchen-middens and the lake-dwellings of Switzer-



land, the corresponding bones being absent in all. Professor Steenstrup "thought that these curious results might perhaps be referred to dogs; and on trying the experiment, he ascertained that the bones which are absent from the Kjökkenmöddings are precisely those which dogs eat"\* . Whether the absence of these particular bones can in the present instance be entirely ascribed to the selective propensity exhibited by the dog, or not, might be somewhat difficult to determine. At any rate we have conclusive evidence that the dog was then an inhabitant of the district; and the gnawed appearance presented by some of the ox-bones show clearly enough that his bone-loving proclivities were as strong in ancient times as they are now.

The bones of the dog, moreover, were found mixed promiscuously with, and very likely had undergone the same culinary operation as, those of his larger and smaller contemporaries; for, like them, he appears to have occasionally filled a corner in the larder of his rapacious masters. At the same time it seems not unlikely that the absent bones may have been pounded in some kind of mortar in order to extract the animal juices—a custom which is still practised by some savage tribes; and if this custom prevailed here during the mound period, doubtless it would be the more nutritious portions of the bones that would be selected for the purpose. With very few exceptions, all the long bones of the oxen have been split open for the purpose of getting at the marrow, and in most cases they are broken transversely. Some of the bones show the marks of two or three blows struck by a blunt instrument in order to split them open. The lower jaws have been broken apparently transversely by the angle of the ramus, and about the middle of the teeth, after which they have not unfrequently been split open in order to get at the fluid contents of the maxillary cavity. The following Table contains the measurements of the bones of the large and the small Ox, so far as their imperfect condition admits of their determination. With these are given the measurements of the corresponding bones of the Ox of the lake-dwellings of Switzerland as given by Rütimeyer†, and those of the lake-dwellings of Italy as given by Gastaldi and translated by Chambers‡. The description of the parts measured are taken from the latter writer.

\* Lubbock, 'Prehistoric Times.'

† *Fauna der Pfahlbauten der Schweiz.*

‡ Lake Habitations and Prehistoric Remains of North and Central Italy.



Parts, measured in millimetres.	Cow of the turbaries, Switzerland.	Ox of the marl-beds, Italy.	Ox of the shell-mound, St. Andrews.	Large Ox of the turbaries, Switzerland.	Large Ox of the shell-mound, St. Andrews.
Circumference of horn-core at base.	120-155	140	125-130	130-182	176-190
Diameter of base (vertical) .....	34-43	36	30-32	39-51	49-54
" " (horizontal) .....	43-55	50	39-48	42-64	58-63
Height of jawbone before first premolar .....	.....	27-36	33		
Molars (second), long .....	.....	20	22		
" " broad .....	.....	13	15		
Premolars (second and third united), long .....	.....	34	34		
Humerus, breadth of trochlea .....	70-73	58-72	61		
Metacarpus, greatest length .....	179-182	162-190	170		
" diam. of upper tuberosity. ....	45-50	45-49	50-55	68-69	62
" " the trochlea .....	46-53	45-50	48-50	68	62
" " the diaphysis .....	26-28	23-35	25-26	40-41	35
Astragalus, total length .....	62-65	59-60	56-61		
Tibia, breadth of superficies of articulation with astragalus ...	40	36-43	35-40		
Astragalus, diameter of inferior surface of articulation .....	37-40	35-36	35-39		
Metatarsus, diameter of upper superficies of articulation .....	.....	38-48	43-45		
Metatarsus, diameter of lower superficies of articulation .....	52	43-50	47-52		
Metatarsus, diameter of the diaphysis .....	26	20-26	22-24		

Of the remains of the Horse, there was the posterior part of a cranium ; the anterior part had been broken off transversely in front of the orbital cavities ; the ethmoid bone seems to have been then broken away, apparently for the purpose of gaining easy access to the brain, which appears in this as well as in other animals, to have been a material of considerable importance in the estimation of our savage precursors. Besides this part of a skull, there was dug up the left ramus of a lower jaw, broken across at the symphysis, and containing all the molars in their places. There were likewise pieces of the distal ends of the tibia, and of the metacarpal and metatarsal bones. Two of the large metatarsal bones and some of the phalanges were entire ; with these exceptions, the long bones were all more or less broken ; they had not, however, been so universally split open as those of the ruminants. These bones, so far as they go, certainly indicate that the horse was then much less than our modern species, and with smaller and more delicately formed limbs, which would undoubtedly have rendered it unsuitable for most of the purposes to which the horse is usually applied at the present day. In size and proportion it seems much nearer the fossil species (*Equus fossilis*) than any of the existing races in this country ; and compared with them,

the antero-posterior diameter of the third molar is in a similar proportion greater than the transverse, although not to the same extent as that of the molar from Oreston, figured by Owen\*. The portions of the skull and jaw found are not so large as the same parts generally are in the common horse; still they are large in comparison to the size of the limb-bones. No doubt it might seem erroneous to affirm that the skull, or jaw, and any of the other bones had belonged to the same individual; at the same time, as they were found within a few yards of each other and in a like condition, we may be allowed to consider them meantime as representative of the race, which may be regarded as a horse with small legs and a large head, resembling the fossil as well as the wild species.

	millims.
Length of metatarsal bone (Horse) . . .	260
Least circumference of shaft . . . . .	88

The bones of the Pig consist for the most part of pieces of the cranium, of the upper and lower jaws (containing some of the molar and other teeth), and a number of fragments of the leg-bones. All these bones, with one exception, have belonged to a small race of pig, closely resembling in size Rüttimeyer's "Torfschwein," or Pig of the Turbaries, an animal very considerably less than the wild boar, of the remains of which I could find no trace, with the exception of a single fragment of a canine tooth. This is the more remarkable, because, according to tradition, the wild boar was common in this district in the early centuries of our era, and Alexander I. conferred upon the see of St. Andrews the famous tract of land called the *Cursus Apri*, or boar's chase, which is supposed to have extended from St. Andrews inland some four or five miles, and perhaps seven or eight miles across the country. The wild boar, from his strength and ferocity, would no doubt be the most conspicuous, although not the more useful animal of the two, and was very likely able to retain his freedom long after his smaller relative was subdued. However this may be, I am persuaded that it will yet be found that this small race of pig was far more numerous, judging from its remains, than the larger species, and at a period far beyond the reach of the most ancient tradition itself. This will be found to be the case, I think, whenever the animal remains met with in and around the various tumuli, cairns, &c. receive more attention than has heretofore been generally bestowed upon them, and when the determination of the species or variety of animals whose remains they contain shall be considered a matter of primary importance, and receive that attention which the interest

\* British Fossil Mammals.

of the subject justly demands. This must be done if we expect ever to arrive at anything like a correct knowledge of the kind of animals that surrounded man in the so-called ages of stone and bronze, and of the relation in which they stood to him, whether domesticated or wild, or if we would form any idea of the social and intellectual condition of man himself—whether in those ages he led the life of a mere savage whose existence depended upon the success of the chase, who starved one day and gorged the next, or whether he possessed the prudence and forethought necessary to manage domesticated animals and utilize them so as to meet his ever-recurring wants. These and other questions connected with the early condition of man in this country can only be solved by strictly examining and, as far as possible, identifying the animal remains, not of the shell-mounds only, but of the tumuli and cairns. I am the more impressed with this, because all the bones of the pig from tumuli and old burying-places that have come into my hands have pertained to a small race. To give one instance: some years ago a group of cinerary urns, each containing calcined bones, were discovered near St. Andrews. In one of the trenches dug at this place a mass of broken bones of different animals was turned up; amongst them there were a considerable number of bones of the pig, and they appeared to me without an exception to belong to a small race. Some of these remains presented the same marks of domesticity as those forming the subject of the present notice, so far at least that the crowns of the third molars were much worn down: this is said by Rüttimeyer to be a reliable mark in determining whether the pig to which they belonged had been in an independent or in a domesticated state. The following measurement will show the relative sizes of the teeth of the pig of this mound and those of Rüttimeyer's pig of the Turbaries and Gastaldi's of the marl-beds:—

Upper maxillary.	Small Pig of the Tur- baries.	Typical Pig of the Tur- baries.	Pig of the marl-beds.	Pig of the shell- mound of St. An- drews.
Length of three molars together.	60-67	65-77	63	60-63
"    third molar alone.....	26-34	30-40	29	26-30
"    molars 2 and 1, and premolars 4 and 3. }	56-60	59-68	60	57

Of the bones of the Sheep, we have part of a cranium, which, like that of the Horse, has been broken across by the orbits. The greater part of the occipital has been torn away, and the horn-cores are broken off near the roots. There is also a piece of a lower jaw containing the molar teeth. Besides these frag-



ments, there are a number of pieces of the bones of the lower limbs of a small ruminant, consisting chiefly of the lower ends of the tibia, of the metacarpal and metatarsal bones, and some of the phalanges. The humerus and femur were absent. That these are bones either of the sheep or goat there can be no doubt; but whether they belong to one or both species is a question that will scarcely admit of a very decided answer. The difficulty of distinguishing the bones of the sheep from those of the goat when in a detached state is well known. The difficulty, however, is still greater in cases like the present, when it is pieces only of the bones we have to deal with, and these pertaining to a remote period, when the sheep and the goat appear to have resembled each other more closely than our domesticated breeds do at present. Moreover the sheep of the shell-mounds and of the lake-dwellings had horns like the goat; while both animals, more especially the sheep, had the limbs relatively longer and smaller than in existing races. Presuming, in the meantime, that the most of these are the bones of a small and perhaps half-domesticated race of sheep with goat-like horns, as shown by the fragment of skull already noticed, and which it may be remarked that, although rather less, it agrees closely with Rüttimeyer's figure of the skull of the "Schaf aus dem Oberland von Graubünden," which he thinks may be the descendants of his "Torfschaf," or sheep of the lake-dwellings. A similar race of sheep is said to be still preserved in some of the Shetland and Orkney Islands. According to Gastaldi, sheep with goat's horns are also to be met with in the island of Cyprus. Beside these bones that we have ascribed to the sheep, there are a few others which, although they do not differ materially in size or shape, are of a closer and harder texture, and have altogether a smoother and more polished aspect, with the muscular ridges sharper and better defined. These I think may with some probability be set down as the bones of a small goat.

The relics of the Dog, although not numerous, are characteristic enough: they comprise a number of the molar and canine teeth and pieces of the bones of the legs, all more or less broken; the lower end of the humerus is the only joint quite entire. These bones indicate a somewhat large dog with rather powerful limbs, perhaps an animal larger than the general size of our shepherd's dogs. The bones are too imperfect to admit of comparison with the measurements given by Rüttimeyer of the bones of his "Torfhund," which, he considers, resembled the "Jagdhund" and the "Wachtelhund." I infer, however, that the bones in question have belonged to a larger race than his "Torfhund," which Lubbock says "was of middle size, and appears to have resembled our present beagles." It seems to



have been larger, too, than the race of dogs that have left their remains in the marl-beds of Italy.

The bones of the Fox were scarcer than those of the Dog ; otherwise they were in much the same condition. So far as the evidence afforded by a few bones; nearly all broken, can be relied on, it seems that the Fox of the period was somewhat less than the present species, as may be seen from the subjoined length of the tibia, the only bone entire, compared with the length of the tibia of the common fox :—

	millims.
Length of tibia of fox . . . .	132
"      "      present fox . .	155

It may be remarked that the fox of the lake-dwellings, according to Rüttimeyer, was also smaller than the present species.

Of the Cat there were only three bones unbroken ; they consist of a humerus, an ulna, and a radius : the humerus and ulna are those of the right side, and may be of the same individual. The radius, from its length, has apparently belonged to a larger specimen. From their size and muscular ridges it is clear that they are the bones of a larger and stronger species than the domestic cat, which is said not to have been known in Europe until about the ninth century. The following are the lengths of the bones :—

	Common Cat. millims.	Shell-mound Cat. millims.
Humerus: from edge of inner condyle to over the head . . . .	85	95
Radius . . . . .	81	93
Ulna . . . . .	97	104

The remains of the Deer admitting of identification consists of a piece of a large horn considerably thicker than the horn of the present red deer ; one end of it bears the marks of numerous blows struck by a cutting instrument. The cuts are oblique, but appear to have been deep enough to admit of the horn being broken in two. The bones of the birds are all those of large species : one or two of them appear to be parts of the shafts of leg-bones ; another is the proximal end of an ulna, and has pertained to a bird somewhat larger than the Eider duck.

## PART II.

Having in the first part of this paper briefly described the animal remains found associated with stone implements and pottery in the shell-mound at St. Andrews, it is now of importance to direct attention more fully to the nature of these imple-

ments and pottery than was compatible with the scope of the previous part of the paper.

The stone implements are formed chiefly of clay-ironstone, a rock common nearly everywhere (along the shore, and where the sedimentary rocks crop out) in this locality. The specimens showing any appreciable design or shape are few in comparison with the great number of broken stones and chips, which, in most cases, are neither more nor less than pieces of stone broken, many of them, to a sharp edge; and although evidently broken by the hand of man, they are in general so destitute of form, that one would think, if they were intended for use at all, that at best it would be the sharp edges only that could be of much service: these, of course, might be applied to various cutting-purposes, as seems to be still the practice of some savage tribes. And it is very likely that a considerable number of these fragments are merely the refuse left from the manufactory of a better-shaped class of weapons. However this may be, there are about a dozen specimens made of the same material, which, although rudely enough formed, evince a certain degree of care and skill in breaking and chipping them into the requisite shapes. None of these objects have been polished; but most of them have undergone a grinding or rubbing process, extending an inch or so up from the cutting edge, which it was meant, no doubt, to improve. The grinding appears to have been sometimes confined to one side of the implement. Some of the specimens, however, are so much corroded, pieces about  $\frac{1}{8}$ th of an inch in thickness having scaled off them, that it is impossible to say with certainty whether they have been ground to an edge on both sides or not. The largest of these articles, which seems to be of the usual chisel shape, is 5 inches in length, and  $1\frac{3}{4}$  inch in breadth. One of the smaller kind (fig. 1, Plate V.) is 3 inches long by  $\frac{3}{4}$  inch in breadth, and is hollowed or ground out at the cutting edge in the form of a gouge. Fig. 2 is another of the chisel forms; it is  $3\frac{3}{8}$  inches long by 1 inch broad at the cutting edge, which is rounded. This specimen has split in two. Fig. 3 is  $2\frac{3}{4}$  inches long by 1 inch at broadest, and is bevelled off obliquely at the cutting edge. Fig. 4 is 2 inches long, at broadest part  $1\frac{1}{4}$  inch; it is concave at the cutting edge, and is hollowed out toward the edge on both sides. Fig. 5 is thin, blunt, and circular at the lower end, and has the body of the implement rubbed or ground to a nearly round form; it is  $2\frac{1}{2}$  inches long. Fig. 6 is  $2\frac{3}{8}$  inches long, and is of the human canine tooth form, but is somewhat blunt at the cutting edge, and tapers away to a sharp point at the upper end. Fig. 7 is  $2\frac{3}{4}$  inches long by  $1\frac{1}{2}$  inch broad at the edge, which is straight transversely. Fig. 8 is  $2\frac{1}{2}$  inches long,  $2\frac{1}{4}$  inches where broadest; it is nearly flat on

one side, round on the other, and has both edges concave. Fig. 9 appears to be part of an axe; it is of a triangular shape, and is  $3\frac{1}{2}$  inches broad at the cutting edge, and at the point where it is broken across (about  $3\frac{1}{2}$  inches from the edge) it is  $1\frac{1}{2}$  inch broad by  $1\frac{3}{4}$  inch thick. Fig. 10 represents one of the thin disks of stone with a small hole pierced in the centre.

There are two or three objects made of greenstone; one of these has been broken to a conical point, and may have been used as a mallet, fixed into a handle. Another of these greenstone articles has been chipped into a round form, and in size is not unlike the handle of a modern knife.

That the Ancient Britons possessed some other and better implements than those under consideration, is, I think, possible enough. Steenstrup is of opinion, according to Lubbock\*, that the mound-builders of Denmark had likewise better implements than those generally found in their middens, and that it is only those things which art could not make available and which were thrown away as useless, or accidentally lost, that we can expect to meet with in these deposits. At the same time, it must be borne in mind that if the people who lived here at the period in question possessed neither flint nor metallic weapons—and there has not been a vestige of any such found,—they must have laboured under difficulties to a great extent unknown to the Ancient Danes or any other people living in a flint-producing country. Clay ironstone, or any other kind of stone in this district, is not nearly so easily made into useful implements as flint is; and they must have been very inferior in their cutting-properties after they were made. The nearest place from which flint could be obtained in any abundance is on some parts of the coast of Yorkshire, a distance too great perhaps for the limited resources of the ancient people to surmount; and under the circumstances it would appear that they endeavoured to do the best they could with the unpromising material at their disposal.

All the pottery was in fragments when found, with the exception of one vessel, which occurred in digging the foundation of one of the houses; and this example, unfortunately, was broken in pieces by the workmen before it was removed from the ground. The specimen (see woodcut) has since been restored to its original form, so far at least as the fragments will admit. It is 9 inches in height by 8 inches at the greatest horizontal diameter; it is of a yellowish or cream colour, easily scratched with a knife; and what remains of the bottom shows clearly enough that that part had been round on the outside, so that it would be impossible to make the vessel when entire stand upright on a level surface. It

\* Prehistoric Times.



likewise exhibits bulges and an inequality of thickness of the walls sufficient, I think, to militate against the idea of its having been shaped on a wheel. The handle is not genuine, but has been restored from pieces of the handles of other vessels\*.



Of the numerous fragments of pottery met with, it is to be regretted that none are large enough to admit of a positive statement as to what had been the prevailing size and shape of the rest of these ancient vessels. There is one piece of the side of a vase, however, that may assist us in arriving at something like a near approximation to the size and shape of some of them at least. This fragment has belonged to a vessel evidently of a somewhat globular form, having a diameter at the mouth of about 9 inches, from which it bulges out downward till it attains a diameter of nearly 12 inches, whence it appears to have contracted inwardly. There are a considerable number of the bottom pieces of these vases; and although all are more or less broken, they show in general a diameter of about 6 inches. If we were to assume that the vessel under consideration had a like diameter at the bottom, thus restored it would be a vase with a diameter at mouth of 9 inches, at bulge 12 inches, at bottom 6 inches, the height about 9 or 10 inches, with the lip projecting externally, and the proportions and shape such as may be occasionally met with in ancient pottery. The most, if not the whole, of this pottery has been hand-made; the irregular thickness of the walls and its rude unsymmetrical appearance sufficiently attest this. There are two or three pieces, however, which, although too fragmentary to allow of a very decided opinion being pronounced

\* I am indebted to Dr. M<sup>r</sup> Kintosh for permission to describe and figure this vessel.



either way, still appear to me to exhibit a greater regularity of the concentric marks on their surfaces, than might perhaps be expected to occur on hand-made pottery. In these cases the potter may have used, if not a wheel, a mould or gauge of some kind to assist him in giving a more regular shape to the better class of vessels. This ware varies from a yellowish to a blackish colour; some examples are brown on the outside and inside surfaces, and have the interior paste almost black. Some, again, are brown on the outside, and the paste and inside black, while other pieces are of a blackish colour throughout. All this earthenware has been made of very coarse clay full of small stones, some of them one-fourth of an inch or more in size, and from their number they give a rough, and in some cases a porous-like appearance to the fractured edges. There were a number of pieces of handles found; and from the size of some of them it is evident that they had pertained to vessels of considerable dimensions. Most of the handles are punctured in a very irregular manner, the holes often extending right through; this is the only ornament observable on any of the fragments, if ornament it can be called. From the irregular way in which this has been performed, and from the brims of some of the utensils where the walls are thickest being punctured in a similar style, it is just possible that it may have been intended as much to assist the baking as to improve the look of the vessel. One of the bottom pieces of a vase bears the impression of the potter's fingers very distinctly on the lower side; the fingers seem to have been small. According to Birch\*, finger-marks are not unfrequently met with on old Celtic pottery. Two or three of the shards have here and there patches of a greenish-coloured glaze on their surfaces, this appears to be the result of vitrification; for there is generally a small hole about the middle of each patch, out of which the vitrifying matter seems to have bubbled during the process of baking. Miss Meteyard†, speaking on this subject, says, "In Scotland, where rocks abound, mica or other fusible matter might be present in clay of which vessels had been formed, and yet be unperceived till, in some solitary instance, partial vitrification had ensued from a higher degree of heat during firing."

It is now necessary to say a few words touching the probable antiquity of this mound, so far as the remains found in it and their condition seem to warrant. It may be observed that the species of animals are not numerous in this mound when compared with those of the Danish mounds and the lake-dwellings of Switzerland, although the bones were broken apparently in a similar manner. Whether this has been done by people

\* Ancient Pottery.

† Life of Wedgwood.

belonging to the same or a different race may not be easy to determine; at any rate it indicates that in habits and customs they had much in common. Still, irrespective of other matters, competent judges tell us that there are not remains of domesticated animals found in the Danish middens; we are therefore bound to consider them the oldest deposits of the kind yet discovered. During the earliest of the lake-dwellings, however, several animals are said to have been domesticated, such as the Ox, Pig, Sheep, Dog, &c. These are the animals, it will be observed, whose bones were found in the greatest number here; not only so, but the small Ox (*Bos longifrons*) appears to have been as common during the period of the oldest of these lake settlements as it was at St. Andrews. Lubbock says of the oxen\*, "the third or *longifrons* race is by far the most common of the three. It occurs in all the Pileworks, and at Moosseedorf and Wangen (that is to say, in the settlements which are supposed to be the oldest), almost to the exclusion of the *primigenius* race." To these lake-dwellings, it appears to me, the St. Andrews mound makes a near approach in point of antiquity. Of course before a like antiquity can be satisfactorily established, other and more extensive investigations will require to be made in our Scottish mounds on other parts of the coast. And perhaps all that can be safely said on the present evidence is, that, if the deposits are not contemporaneous, that of St. Andrews is certainly the refuse of a race at all events not further, if so far advanced in civilization as the lake-people of Switzerland. Shell-mounds were discovered some time ago at two or three other places on the eastern coast of Scotland, although, as yet, they are not numerous, and some of them not very productive; but as attention is now directed to the subject, we may by-and-by expect to hear of others. Meantime those of the Moray Firth are described by Sir J. Lubbock†. They consist of a mass of shells and pieces of bones intermixed; the shells, like those of St. Andrews mound, were chiefly littoral species. The animals determined were the Ox, Sheep, and Pig; what species, or whether they appeared to be domesticated or not, is not stated. Lubbock says, "We did not find any implements or pottery, although we searched for several hours; but a labourer in carting it away for manure had previously found some fragments of rude pottery and a bronze pin." The pin is supposed, from its workmanship, to be of the eighth or ninth century: if this is taken as an indication of the age of the deposit, it would make the latter more recent than we should consider that of St. Andrews to be. The shell-mounds of Caithness are described

\* Prehistoric Times.

† Natural History Review, 1863.

at considerable length by Mr. Laing\*: the animals in the list given by him are similar to those met with here; the main exception seems to be the bones of two or three species of cetaceous animals. There was only one species of ox, however, the *Bos longifrons*; and the horse is described as a large-headed animal of small size, but considerably larger than the Shetland pony, corresponding perfectly with the *Equus fossilis*. Mr. Laing appears to be of opinion that none of the animals had been in a domestic state, with perhaps the exception of the dog. Should this be the case, then they would be considered of greater antiquity than the remains met with in the mound at St. Andrews. As already observed, however, more extensive researches are necessary before we can arrive at any reliable conclusions as to the relations of the Scottish mounds to each other, as well as to the continental deposits. There is another matter in connexion with shell-mounds on which I would venture to say a word or two: some people appear to hold the opinion that if a mound is found to contain the bones of domestic animals, such as the Ox, Pig, Horse, &c., it is very likely an accumulation of recent date, and not entitled to rank as a prehistoric deposit at all. While this may in some cases be quite true, yet if it was to be generally acted on, and no mound examined that was found to contain the skull of a horse or the horn-core of a cow, it might be the means of depriving us of much valuable information, because the most, if not all, of our domestic animals of that class are in all probability neither more nor less than the descendants of those races whose bones we find in the recent (geologically speaking) clays and gravels of the country. Besides, we do not appear, during the whole of the historic period, to have succeeded in adding a single quadruped to the list of our domesticated animals. All the animals of that kind worthy, or, at all events, capable of being domesticated, were brought into that condition long before the historic era of Western Europe at any rate. We have no doubt improved the breeds of our animals, and of course to some extent modified their structure by means of artificial selection. Nevertheless it is an open question whether we have done more than merely improve a race of animals who have descended to us in a domesticated state from the men of the Neolithic age in Europe.

\* Prehistoric Remains of Caithness. I am aware that some of Mr. Laing's conclusions have been called in question; but as the bones were identified by competent authorities, there cannot be any mistake about them.



XLIII. *On the Dispersion of Light in Gases.*

By Dr. KETTELER\*.

THE livelier the interest becomes which is now taken in the search after the laws whereby the propagation of light is connected with the density and chemical composition of the medium in which it moves, the more firmly shall we be convinced that it is only through a comprehensive study of the phenomena of refraction and dispersion in gaseous bodies that the discovery of comparatively simple laws is possible, and that the true path by which to approach the incomparably more complex case of solid and liquid bodies lies through these. I have therefore undertaken to submit the refracting and dispersive powers of gases to a more accurate investigation. The essential parts of the physical portion of this investigation are already completed, and I therefore communicate in the following pages the results that have been arrived at.

Thanks to the method I adopted, I have succeeded in determining with precision the indices of refraction of the gases for the separate Fraunhofer's lines, and in ascertaining the law which connects these indices with the density. I have indeed abandoned the method of prismatic analysis, which has hitherto been adopted almost exclusively, and based my apparatus on the principle of interference. If it be borne in mind that the excess of the index of refraction above unity, which becomes in the interference method the object of direct observation, is, according to the older experiments of Arago and Biot, proportional to the density—if it be considered, further, that the advantage just mentioned is of still greater importance in the study of dispersion, since exact coincidences of differently coloured fringes are very easily established, and are moreover comparatively little affected by changes of form in the closing plates, whereas the accurate adjustment of an instrument upon the lines of a spectrum whose entire length is measured by seconds must be nearly impossible, it will be admitted that the method that has been adopted is the only appropriate one. Sources of homogeneous light of various colours were of course necessary; and the fringes had to be followed, when needful, by thousands, without the interposition of compensators. It will be seen that such a mode of operating could not have been practically available but for the discovery of Professors Bunsen and Kirchhoff.

The following experiments were made for the most part in the new Institute of Natural Science at Heidelberg, where Professor Kirchhoff most liberally placed at my disposal the requisite space and apparatus, without which this difficult investigation would not have been possible.

\* Translated from Poggendorff's *Annalen*, vol. cxxiv. p. 390, with corrections communicated by the Author.



The complete determination of the optical properties of the gases required a connected and uniform measurement of all the elements concerned. In the first place it was needful to measure more accurately than had hitherto been done the wave-lengths of the three sources of homogeneous light which I employed, namely the lithium-, sodium-, and thallium-flames. For this purpose the method recommended by Fizeau\* was followed. This consists in finding the coincidences which occur when an appropriate system of Newton's rings is illuminated by each pair of the above-mentioned flames simultaneously. By help of an apparatus in which the plates needed to produce these rings were contained—the upper one being fixed but so arranged as to be capable of assuming any required inclination to the lower one, while the latter could be moved vertically up and down, without the slightest twisting, by means of a lever worked by a micrometric screw—the number of rings intervening between two coincidences could be observed: the following, for instance, are examples of numbers actually thus obtained:—

$$\frac{\mu_{\text{Na}}}{\mu_{\text{Li}}} = \frac{1156}{1015}, \quad \frac{\mu_{\text{Tl}}}{\mu_{\text{Na}}} = \frac{770}{699}, \quad \frac{\mu_{\text{Tl}}}{\mu_{\text{Li}}} = \frac{1537}{1225}.$$

The delicacy of the apparatus was such that, in moving the lever, the finger had to pass over a length of more than 10 millimetres in order to cause a displacement to the extent of a single fringe. As the mean of twenty-three observations of this kind, the following ratios were obtained:—

$$\frac{l_{\text{Li}}}{l_{\text{Na}}} = 1.138953; \quad \frac{l_{\text{Na}}}{l_{\text{Tl}}} = 1.101568; \quad \frac{l_{\text{Li}}}{l_{\text{Tl}}} = 1.254638.$$

The product of the first two numbers gives 1.254634.

In order to obtain the absolute values of the wave-lengths, we must adopt for  $l_{\text{Na}}$  Fraunhofer's value = 0.0005888 millim., inasmuch as Fizeau's contemplated repetition of this measurement has not yet been published, and to determine it myself lay beside the scope of my investigation. We thus obtain, in hundred-millionths of a millimetre,

$$l_{\text{Li}} = 67061.6, \quad l_{\text{Na}} = 58880.0, \quad l_{\text{Tl}} = 53451.0,$$

numbers which may be regarded as relatively tolerably certain, as far as the fifth place.

It was now possible to proceed to the determination of the dispersive properties of gases. The gases examined were the five following:—air, carbonic acid, hydrogen, cyanogen, and sulphurous acid.

The gases were placed in tubes between thick interference-plates, such as those introduced and several times described by

\* *Annales de Chimie et de Physique*, 3<sup>e</sup> sér. vol. lxvi. p. 429.

Jamin\*, which produced fine and easily traceable systems of fringes. A Geissler's mercurial air-pump† was used in filling the tubes, and in order to compress or rarefy the gases a second pump, consisting of a metal cylinder in which there moved, with as much friction as possible, a piston capable of being slowly and continuously screwed in or out by a proper contrivance. The changes of pressure were read off by a cathetometer, on a manometer consisting of glass tubes 15 millims. wide. The pressure could be augmented, if required, from its ordinary amount to four atmospheres. The plan of the investigation now was, starting from a first coincidence, with mixed light (for instance, red and yellow), and gradually augmenting the pressure, to find the second, third, &c., noting at the same time the corresponding readings of the manometer.

The first experiments, however, which were made with air, greatly simplified the process. Successive series of bands, which coincided most accurately with each other, were found for the three possible combinations of colour, namely—

Yellow : Red.		Green : Yellow.	
$\frac{8}{7} =$	1·14286	$\frac{21}{19} =$	1·10526
$\vdots$		$\vdots$	
$\frac{104}{91} = \frac{8}{7} \cdot \frac{13}{13} =$	”	$\frac{73\cdot5}{66\cdot5} = \frac{21}{19} \cdot \frac{3\cdot5}{3\cdot5} =$	”
$\vdots$		$\vdots$	
$\frac{200}{175} = \frac{8}{7} \cdot \frac{25}{25} =$	”	$\frac{147}{133} = \frac{21}{19} \cdot \frac{7}{7} =$	”
$\vdots$		$\vdots$	
$\frac{304}{266} = \frac{8}{7} \cdot \frac{38}{38} =$	1·14286	$\frac{315}{285} = \frac{21}{19} \cdot \frac{15}{15} =$	1·10526
Green : Red.			
$\frac{24}{19} =$	1·26316		
$\vdots$			
$\frac{240}{190} = \frac{24}{19} \cdot \frac{10}{10} =$	”		
$\vdots$			
$\frac{336}{266} = \frac{24}{19} \cdot \frac{14}{14} =$	1·26316		

\* *Ann. de Chim. et de Phys.* 3<sup>e</sup> sér. vol. lii. p. 166.

† Meyer, *Beobachtungen über das geschichtete elektrische Licht*, Berlin, 1858.



and here expresses the ratio of the shortening of the wave-lengths corresponding to two definite times of vibration, may henceforth be regarded as a measure of the amount of dispersion. According to this, the dispersive force must be independent of the density, and essentially connected with the properties of the molecules.

For the sake of perspicuity, I have collected in the following Table the whole of the observations made upon the above-mentioned gases:—

To 10,000 red bands correspond—	Yellow Bands.	Green Bands.
When one of the interfering rays is geometrically retarded by the lengthening of its path in air . . . .	11389·53	12546·36
When one of the interfering rays is physically retarded by increase of density in		
Air and carbonic acid gas . . . .	11428·6	12631·6
Hydrogen . . . . .	11441·4	12659·6
Cyanogen . . . . .	11460·5	12698·1
Sulphurous acid gas . . . .	11463·4	12705·7

If the numbers of the second column are calculated from those of the third, as they easily can be (see below), the mean difference between calculation and observation amounts to about seven units in the sixth place.

The great dispersive power of hydrogen is especially interesting.

It now only remains to determine the indices of refraction for some one colour (for example, that of the sodium-light) in order to know them for the two other colours also. For this purpose, experiments were made in which the increase of pressure corresponding to the displacement of every twenty-five bands was observed.

The following results obtained in this manner with air are given as examples:—

$m$ .	$p_1$ .	$p_2$ .	$\frac{p_1}{m}$ .	$\frac{p_2}{m}$ .	Temperatures.
	millims.	millims.	millims.	millims.	
0	— 0·33	— 0·98			
25	+99·09	+98·78	3·9784	3·9644	At the beginning:—
50	199·42	198·92	3·9966	3·9962	Tubes ..... 18°·35
75	299·19	298·71	3·9952	3·9941	Manometer 18°·42
100	399·01	398·62	3·9950	3·9943	
125	498·85	498·30	3·9950	3·9925	At the end:—
150	598·34	598·27	3·9927	3·9933	Tubes ..... 18°·60
175	697·76	697·58	3·9906	3·9901	Manometer 18°·50
200	797·58	.....	3·9911		

The column headed  $m$  gives the number of bands, and the columns headed  $p$  the corresponding excesses of pressure, the



pressures  $p_1$  being observed as the pressure was increasing, and  $p_2$  as it was falling. The quotients  $\frac{p}{m}$  (neglecting the two first) are perfectly constant, with the exception of a slight decrease, which is sufficiently explained by conditions of temperature of the various parts of the apparatus.

As a mean value for the indices of refraction, I obtained, from two only slightly differing experiments with common air, the following number applicable to the temperature  $0^\circ$  C. and the normal barometric pressure:—

$$n_{Na} = 1.00029470,$$

a result which is quite accordant with those previously given by Delambre, Arago, and Biot.

Hence we get also

$$n_{Li} = 1.000293669,$$

$$n_{Na} = 1.000294704,$$

$$n_{Ti} = 1.000295669.$$

By multiplying these numbers into the above-given wave-lengths, we obtain, lastly, for the wave-lengths in space free from air and destitute of dispersive power, the values

$$\lambda_{Li} = 67081.2, \quad \lambda_{Na} = 58897.3, \quad \lambda_{Ti} = 53466.8.$$

For what relates to the indices of the other gases, I must refer to my complete paper, published separately under the title "Observations on the Chromatic Dispersion of Gases" (*Beobachtungen über die Farbenzerstreuung der Gase*): Bonn, 1865.

### Supplement.

To the foregoing communication, which was printed in the Monthly Notices (*Monatsberichte*) of the Royal Academy of Berlin for the year 1864, I thought myself justified in adding a formula which expresses the index of refraction as a very simple function of the wave-length and density, and whose two constants retain approximately the same value for all states of aggregation of one and the same substance. The equation in question was

$$n^2 - 1 = a \frac{1}{1 - \frac{\beta^2}{l^2}},$$

where  $l$  denotes  $\frac{\lambda}{n}$ , and  $A (= a)$  and  $\beta^2$  are constants, and  $\beta = \lambda_0$  may be regarded as a wave-length.

But continued and very comprehensive calculations have determined me to replace this formula by the following:—

$$n-1 = \alpha \frac{1}{1 - \frac{\beta^2}{\lambda l}} \quad \text{. . . . . (III)}$$

If we here also put  $\beta = \lambda_0 = VT_0$ , where  $V$  stands for the velocity of light in a vacuum, and  $T_0$  for the time of vibration, and if  $l = v_0 T_0$  be regarded as the internal wave-length connected with  $\lambda_0$  by the index  $n_0 = \frac{V}{v_0}$ , equation (III) takes the following form:—

$$\frac{n-1}{n_0-1} = \frac{\frac{\lambda}{\lambda_0} - \frac{\lambda}{l_0}}{\frac{\lambda}{\lambda_0} - \frac{\lambda}{l^0}},$$

or

$$\left(1 - \frac{v}{V}\right) \left(\frac{T_0^2}{T^2} - \frac{v}{V}\right) = \left(\frac{v}{v_0} - \frac{v}{V}\right)^2;$$

and since, for  $\lambda = \infty$ , we get  $n_\infty - 1 = \alpha$ ,

$$(n-1) : (n-n_\infty) = \frac{\lambda}{\lambda_0} : \frac{\lambda_0}{l},$$

or

$$\frac{V-v}{v_\infty-v} = \frac{v}{v_\infty} \cdot \frac{T^2}{T_0^2}.$$

If in equation (III) we put  $\frac{\lambda}{n}$  for  $l$  and solve for  $n$ , developing the resulting exponential quantities by the binomial theorem and making the proper reductions, we obtain

$$\frac{n-1}{\alpha} = 1 + (1+\alpha) \frac{\beta^2}{\lambda^2} + (1+\alpha)(1+2\alpha) \frac{\beta^4}{\lambda^4} + \dots *.$$

On the other hand, if  $\lambda$  be replaced by  $nl$ , we obtain the analogous series,

$$\frac{n-1}{\alpha} = 1 + \frac{1}{1+\alpha} \cdot \frac{\beta^2}{l^2} + \frac{1}{(1+\alpha)^3} \cdot \frac{\beta^4}{l^4} + \frac{1-\alpha}{(1+\alpha)^5} \cdot \frac{\beta^6}{l^6} + \dots,$$

Hence we get for the square of the reciprocal of the index of refraction

$$\frac{1}{n^2} = \frac{1}{(1+\alpha)^2} - \frac{2\alpha}{(1+\alpha)^4} \cdot \frac{\beta^2}{l^2} + \frac{\alpha(3\alpha-2)}{(1+\alpha)^6} \cdot \frac{\beta^4}{l^4} - \frac{2\alpha(1-4\alpha+\alpha^2)}{(1+\alpha)^8} \cdot \frac{\beta^6}{l^6} + \dots,$$

an equation which, when the values of the constants have certain ratios, may be reduced to the first two terms.

\* Writing  $n^2$  for  $n$ , this brings us back to the equation first proposed.

Whether and to what extent a special correspondence is discoverable between the several coefficients of this series and those of Cauchy need not now be considered.

It can be shown that the formula (III) does in reality comprehend with great exactness the whole of the phenomena of dispersion that have yet been investigated.

That this equation applies very accurately to the results of observation on the dispersive properties of gases has been already shown above.

The best measurements which we possess of the indices of refraction of Fraunhofer's lines (those, namely, which we owe to Fraunhofer, Rudberg, and Landolt) have been compared with it, and a very good agreement has been found\*. In general the differences are identical with those which result from the application of Cauchy's primary series, as reduced to their first two terms by Christoffel†.

I have myself employed the spectra of lithium, sodium, and thallium in order to measure, as accurately as possible, the indices of refraction of the corresponding lines for a prism of heavy glass. With the aid of a Steinheil's spectroscop, belonging to the physical cabinet of the University of Heidelberg, which was most kindly placed at my disposal by Professor Kirchhoff, I obtained the following indices of refraction:—

$$n_{\text{Li}} = 1.683879, \quad n_{\text{Na}} = 1.691361, \quad n_{\text{Tl}} = 1.698535,$$

numbers which I consider all the more accurate since, in consequence of the small intensity of the sources of light and the short duration of the experiments, all variations of temperature were avoided, as well as because, in the method that was employed of having the prism fixed, the error of the minimum deviation was avoided.

On the other hand, we may calculate from the first and last of these numbers the following value for the second:—

$$\begin{array}{l} \text{By formula (III).} \\ n'_{\text{Na}} = 1.691351. \end{array}$$

$$\begin{array}{l} \text{By Christoffel's formula.} \\ n''_{\text{Na}} = 1.691356. \end{array}$$

So that, in units of the fifth decimal place, the difference  $n - n'$  amounts to 1, and the difference  $n - n''$  to 0.5. In view of the sources of experimental error, these differences may obviously be regarded as inconsiderable.

Lastly, as to the quantity  $\beta = \lambda_0$ , it is of the same order for gases, liquids, and solids; thus, for example, calculation gives:—

\* Much better than when the earlier formula was used.

† Poggendorff's *Annalen*, vol. cxvii. p. 27.

		millim.
For	{ Air . . . . .	$\lambda_0 = 0.0000723$
	{ Hydrogen . . . . .	$= 0.0000831$
	{ Cyanogen . . . . .	$= 0.0000958$
"	{ Water . . . . .	$= 0.0000813$
	{ Sulphide of carbon . . . . .	$= 0.0001235$
„	Heavy glass . . . . .	$= 0.0000959$

The idea consequently easily suggested itself that this quantity might remain strictly constant for the passage of a substance from one state of aggregation to another, especially as  $\lambda_0$  appears as the wave-length in a vacuum. I have tested this conclusion in the case of sulphide of carbon, and, particularly, in that of sulphurous acid.

After encountering many difficulties, the ratio of the numbers of simultaneously displaced red and yellow bands was found to be, for sulphide-of-carbon vapour  $= \frac{45.5}{39.5}$ ; while the ratio calculated, upon the above supposition, from the constants applicable to liquid sulphide of carbon is  $= \frac{45.5}{39.53}$ .

Liquid sulphurous acid was also submitted to careful measurement. The indices obtained were

$$n_{Li} = 1.33574; \quad n_{Na} = 1.33835; \quad n_{Ti} = 1.34108.$$

For the combination of  $n_{Li}$  and  $n_{Ti}$ , formula (III) gives

$$\lambda_0 = 0.00009404 \text{ millim.}, \quad \alpha = 0.32692,$$

and hence

$$n'_{Na} = 1.33838;$$

and therefore, in units of the fifth place,  $n - n' = -3$ .

The temperature was  $24^\circ.1$  C. Now for *liquid* sulphurous acid we have

$$d = 1.4821 \text{ (Pierre)}, \quad A = \frac{\alpha}{d} = 0.221, \quad \lambda_0 = 0.0000940 \text{ millim.};$$

for *gaseous* sulphurous acid,

$$d = 2.216.0001293 \text{ (Dulong)}, \quad A = 0.225, \quad \lambda_0 = 0.0000981.$$

It will be seen that the two constants remain exactly identical even within these exceedingly wide limits.

In the introduction to this paper I insisted on the importance of the study of the optical properties of gaseous bodies, and declared the method which I have followed to be the only appropriate one. The experiments that have been recorded will, I think, justify this assertion; for the method employed has rendered possible the first successful measurements of the delicate phenomenon of the chromatic dispersion of light in gases, and



the important law, that the dispersive power of a given substance is a property depending rather upon its individual nature than on the more or less dense state of aggregation of its molecules, has thus been established. I reserve to myself to pursue this investigation and to extend it to homologous series.

Finally, as to the formula that has been proposed, I think I have shown that it fulfils its purpose in the simplest and most comprehensive manner. But as long as it does not rest upon any more direct theoretical basis, it may be regarded as a more or less happy expression of the phenomena.

On the other hand, the unexpected result to which the foregoing calculations have led, namely, that in isotropic substances the constants of refraction and dispersion are independent of physical constitution, but essentially connected with chemical characteristics, cannot any longer be doubted. The only exception to the above rule is presented by water, at least within certain limits, inasmuch as its index of refraction increases below  $4^{\circ}$  (according to Jamin and others) as the density diminishes.

I close this communication with a statement of the indices of refraction of air for each one of Fraunhofer's lines:—

$n_A = 1.00029286,$	$n_E = 1.00029584,$
$n_B = 1.00029350,$	$n_F = 1.00029685,$
$n_C = 1.00029383,$	$n_G = 1.00029873,$
$n_D = 1.00029470,$	$n_H = 1.00030026.$

Bonn, January 15, 1865.

#### XLIV. *On the Conversion of Wind-charts into Passage-charts.* By FRANCIS GALTON, F.R.S.\*

THE most direct line between two points of the ocean is seldom the quickest route for sailing-vessels. A compromise has always to be made between directness of route on the one hand, and the best chance of propitious winds and currents on the other. Hence it is justly argued that an inquiry into the distribution of the winds over all parts of the ocean is of high national importance to a seafaring people like ourselves. A knowledge of the distribution of the winds would clearly enable a calculation to be made which would show the most suitable passage in any given case.

But as a matter of fact, no calculations have yet been made upon this basis; much less have charts been contrived to enable

\* Communicated by the Author, having been read at the Meeting of the British Association, in Section A, on August 24, 1866.

a navigator to estimate by simple measurements the probable duration of a proposed passage. The wind-charts compiled by the Meteorological Department of the Board of Trade are seldom used by navigators; for they do not afford the results that seamen principally require; they only give data from which those results might be calculated by some hitherto unexplained process, which, we can easily foresee, must be an exceedingly tedious one.

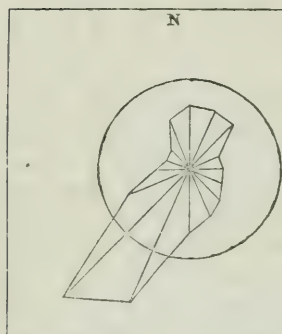
To convert wind-charts, or the tables of wind-direction from which the wind-charts have been compiled, into passage-charts, we must ascertain the distances that ships of different classes would attain in an hour, if they made the best of their way under the same wind towards different points of the compass. With a moderate wind, a merchantman of the class that usually navigates the Atlantic will, by beating to windward, make  $2\frac{1}{3}$  miles an hour, right in the wind's eye. At two points off the wind it will make 3 miles; at four, 4 miles; at six, 7 miles; at eight,  $8\frac{1}{2}$  miles; at ten, 9 miles; at twelve,  $9\frac{1}{2}$  miles; at fourteen,  $8\frac{3}{4}$  miles; and at sixteen, or with the wind right astern, it will make  $7\frac{1}{2}$  miles. We must next turn to the wind-charts, or to the Tables from which they were compiled, to ascertain the proportion of the winds that blow from different points of the compass, in the region we are investigating. Thus in one particular case we find, out of one hundred observations, that six referred to N. winds, fourteen to N.N.E., seventeen to N.E., six to E.N.E., three to E., two to E.S.E., two to S.E., five to S.S.E., six to S., six to S.S.W., six to S.W., three to W.S.W., three to W., three to W.N.W., four to N.W., five to N.N.W., and nine calms. The force of the winds was not recorded in this instance; we must therefore, for want of better information, assume them to be moderate. We have now to calculate the progress that ships could make towards each point of the compass, under the several influences of each of these winds. In the example taken, the N. wind will be reckoned as lasting 6 per cent. of an hour, and therefore ships would be able to sail during its prevalence, .014 mile to the N., .018 to the N.N.E., and so on. The N.N.E. wind lasting 14 per cent. of an hour will enable ships to sail .012 mile to the N., .033 mile to N.N.E., and so on. The N.E., E.N.E., and all the other winds would have their influence similarly calculated. We thus obtain a Table of sixteen lines (not reckoning the line of zeros that correspond to "calms") and of sixteen columns, whose addition gives the total progress of one particular class of ships, in one hour, to all points of the compass, under the influence of the winds that blow in the ocean-district under consideration.

## Method of Calculating Data for the Construction of a Passage-chart.

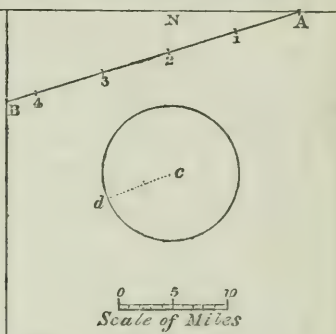
		Corresponding passages in various directions (in nautical miles).															
Hours of wind.	Direction of wind.	N.	N.N.E.	N.E.	E.N.E.	E.	E.S.E.	S.E.	S.S.E.	S.	S.S.W.	S.W.	W.S.W.	W.	W.N.W.	N.W.	N.N.W.
9	Calm.	—	18	—	—	—	—	—	—	—	—	—	—	—	—	—	—
6	N.	14	18	24	42	51	54	57	52	45	52	57	54	51	42	24	18
14	N.N.E.	42	33	42	56	98	119	126	133	121	105	121	133	126	119	98	56
17	N.E.	68	51	40	51	68	119	144	153	161	149	127	149	161	153	144	119
6	E.N.E.	42	24	18	14	18	24	42	51	54	57	52	45	52	57	54	51
3	E.	25	21	12	9	7	9	12	21	25	27	28	26	22	26	28	27
2	E.S.E.	18	17	14	8	6	5	6	8	14	17	18	19	17	15	17	19
2	S.E.	19	18	17	14	8	6	5	6	8	14	17	18	19	17	15	19
5	S.S.E.	44	47	45	42	35	20	15	12	15	20	35	42	45	47	44	37
6	S.	45	52	57	54	51	42	24	18	14	18	24	42	51	54	57	52
6	S.S.W.	52	45	52	57	54	51	42	24	18	14	18	24	42	51	54	57
6	S.W.	57	52	45	52	57	54	51	42	24	18	14	18	24	42	51	54
3	W.S.W.	27	28	26	22	26	28	27	25	21	12	9	7	9	12	21	25
3	W.	25	27	28	26	22	26	28	27	25	21	12	9	7	9	12	21
3	W.N.W.	21	25	27	28	26	22	26	28	27	25	21	12	9	7	9	12
4	N.W.	16	28	34	36	38	35	30	35	38	36	34	28	16	9	9	12
5	N.N.W.	15	20	35	42	45	47	44	37	44	47	45	42	35	20	15	12
Total } hours }	All winds.	530	506	516	553	610	661	679	672	654	632	632	668	686	683	652	589
Or, in one hour.	All winds.	5.3	5.1	5.2	5.5	6.1	6.6	6.8	6.7	6.5	6.3	6.3	6.7	6.9	6.8	6.5	5.9

The bottom line of the Table gives the results that we seek. In the case we have taken, the diagram in the Wind-chart and that in the Passage-chart would be of the following shapes respectively:—

*Wind-chart Diagram.*



*Passage-chart Diagram, calculated from that of the Wind-chart.*



The proportion of winds from the neighbourhood of each of sixteen points of the compass is shown by the length of the corresponding lines drawn to the leeward of the centre. The radius of the circle represents the proportion of calms.

The force of the winds is not given in this diagram. It must therefore be reckoned as "moderate" throughout.

The probable length of an hour's sail in any direction from *c*, the centre of the diagram, is shown by the length of its radius in that direction. This gives a scale to be used throughout the ocean area to which the diagram refers.

*Example.*—Since *AB* is  $4\frac{1}{4}$  times the length of the parallel radius *cd*, therefore the passage from *A* to *B* will occupy on an average  $4\frac{1}{4}$  hours.

We should not be justified in usually adopting an "average force" for the winds, though, for simplicity of explanation, we selected the foregoing example, in which we were obliged to do so. If we confined our computation to the effect of simple averages, then an alternation of squalls and calms would be improperly reckoned as moderate weather. We must therefore group the winds, not necessarily to each degree of force, but, it may be, in two or perhaps three groups. The Tables would therefore consist not of sixteen lines, but of twice or thrice that number. For the rapid performance of these calculations we should tabulate the passages of various classes of ships to each of the sixteen points of the compass, under the influence of winds of, say, thirty different degrees of duration, and six of force, making a total of 180 lines for each class of ships. In each line the figures should be repeated, so as to sweep not only once but twice round the compass. If these are printed on separate slips of paper, the labour of copying them would be wholly avoided; for the same slips



could be used over again. An *extract* from the foregoing Table will suffice for an example of what is meant; where, in order to save space, the figures that refer to the eight principal points of the compass are alone inserted.

		<table><tr><td>N.</td><td>N.E.</td><td>E.</td><td>S.E.</td><td>S.</td><td>S.W.</td><td>W.</td><td>N.W.</td></tr></table>																N.	N.E.	E.	S.E.	S.	S.W.	W.	N.W.
N.	N.E.	E.	S.E.	S.	S.W.	W.	N.W.																		
ours 6	Force mod.	14	24	51	57	45	57	51	24	14	24	51	57	45	57	51	24								
Hours 17	Force mod.	40	68	144	161	127	161	144	68	40	68	144	161	127	161	144	68								
Hours 3	Force mod.	7	12	25	28	22	28	25	12	7	12	25	28	22	28	25	12								
...	Hours 2	Force mod.	5	8	17	19	15	19	17	8	5	8	17	19	15	19	17	8							
....	Hours 6	Force mod.	14	24	51	57	45	57	51	24	14	24	51	57	45	57	51	24							
.....	Hours 6	Force mod.	14	24	51	57	45	57	51	24	14	24	51	57	45	57	51	24							
.....	Hours 3	Force mod.	7	12	25	23	22	28	25	12	7	12	25	28	22	28	25	12							
.....	Hours 4	Force mod.	9	16	34	38	30	38	34	16	9	16	34	38	30	38	34	16							
Total.																									

If the slips were of sufficient length to include the data for every class of ship, a single operation would simultaneously build up Tables for all.

A navigator wishing to find the probable duration of his intended voyage, would refer to a chart on which the results of these calculations had been protracted in the form of diagrams. He must set his compasses to the radius of the diagram nearest to the commencement of his intended route, measuring it in a direction parallel to the route. He will thereby obtain a scale of probable distance for one hour's sail during that part of his voyage, and he will prick out his passage accordingly. When he has come within the range of another diagram he will set his compasses afresh. Continuing on this principle, he will dot out the probable duration of the whole of a proposed passage in the simplest possible manner. He will thus be able to select the quickest out of any number of routes that may be suggested to him, and to determine, on the most trustworthy of existing data, what is the best course to adopt in sailing from any one part of the ocean to another.

The method of altering a diagram so as to include the effect of a current, is too simple to require explanation.

XLV. *Description of a new Proportion-Table equivalent to a Sliding-Rule 13 feet 4 inches long. By J. D. EVERETT, D.C.L., Assistant Professor of Mathematics in Glasgow University\*.*

A LOGARITHMIC scale is a scale of divisions with numbers written against them or otherwise indicated, characterized by the property that equal distances between divisions correspond to equal ratios between the corresponding numbers. With the aid of such a scale, a fourth proportional to any three numbers can be found by measuring the distance between the first and second, and setting off this distance from the third.

The common sliding-rule consists essentially of two such scales, which are perfect fac-similes of each other, one of them being on the solid wood of the rule, and the other on a slidingpiece which moves beside it. In order to find a fourth proportional by means of this instrument, it is only necessary to move the slide until the first and second terms are opposite one another, and the fourth term will then be found opposite the third. Multiplication and division can of course be performed in this way, since they are reducible to proportions in which one term is unity.

Each of the two scales begins with 1 and ends with 100 ; and the first half, which extends from 1 to 10, is precisely similar to the second half, which extends from 10 to 100 ; for the numbers 1, 2, 3, &c. having the same ratios to one another as 10, 20, 30, &c., must be placed at the same distances apart as these latter. In general the division which stands for any one number may also stand for the product or quotient of this number by any power of 10. Each of the two scales may therefore be said to contain all numbers twice over, this repetition being adopted in order to avoid passing out of range when the slide is moved from its initial position.

There is another form in use, consisting of two concentric circles with logarithmic scales placed round their circumferences, the inner circle being constructed to turn about the common centre. In this form of the slide-rule there is no necessity for duplicates, as passing out of range is impossible ; and the complete scale from 1 to 10 is made to extend once round each circumference, the division for 10 being identical with that for 1.

This arrangement effects so great an economy of space as compared with the straight sliding-rule, that it is compatible with the adoption of a much larger scale. In fact the circumferences of the circles may conveniently be made as much as 2 feet, which implies the same size of scale as in a straight rule 4 feet long. This advantage, however, is counterbalanced by some drawbacks, of which perhaps the most serious is the position in which the

\* Communicated by the Author, having been read at the Meeting of the British Association at Nottingham.

figures are written, radiating outwards in all directions like the signatures to a round-robin—an arrangement which prevents the eye from gathering them in easily at one view, and renders it necessary, after the first and second terms of a proportion have been brought into coincidence, to turn the instrument bodily into a different position before the third and fourth terms can be found. This necessity for handling the instrument after it has been set, demands a certain amount of stiffness in the turning of the moveable circle, to prevent unintentional displacement, while, on the other hand, too much stiffness retards the operation of setting; and between these two extremes, with the swelling and shrinking of materials to increase the difficulty, the true mean of convenient working is not often attained.

The new arrangement which we have now to describe is free from these disadvantages, and at the same time permits of a much greater enlargement of scale. Its distinguishing feature consists in breaking up each of the two pieces which constitute a sliding-rule into a number of equal parts, and arranging these consecutively in tabular fashion in parallel columns, the columns on one of the two pieces being visible through openings cut between the columns of the other.

The arrangement of the columns is as follows. One of the two pieces, that to which we shall give the name B, contains an even number of columns, which, if placed in one continuous line in the order of their succession, would form a logarithmic scale in duplicate, like one of the scales of the ordinary sliding-rule.

The other piece, which we shall call A, contains only half as many columns, but these are of double the length. They must be so arranged that the numbers in any one column are consecutive, and that the lower half of any column is precisely similar to the upper part of that which follows it.

In one of these two pieces (it is theoretically indifferent which) openings are cut between the columns, and the arrangement is complete.

It will be observed from this description that the piece called A is twice as high as B, but only half as wide. When one piece is laid upon the other, the portion common to both is a rectangle whose area is half that of either of the pieces; and this rectangle contains on each of the two pieces a complete series of numbers—that is to say, a series proceeding gradually from a certain number up to another ten times as great. All the numbers on one piece have the same ratio to those which stand opposite them on the other; so that we have thus a complete Table of proportional numbers for the particular ratio corresponding to the position in which the pieces have been laid; and this ratio can be made anything we please. It is of course necessary that the pieces be



so placed as to have their columns parallel. In rapid working, this adjustment can be made with fair accuracy at a cursory glance; but in order to enable the operator to make it with the greatest possible nicety, both the pieces are ruled with lines at right angles to the columns, and these lines are placed about a hair's breadth wider apart on one piece than on the other, so that, on the principle of the vernier, one line can always be found which will extend continuously across both.

The arrangement described will be best understood by inspecting the specimen which accompanies this paper\*. The material which has been selected for the pieces is Bristol-board, on which the numbers and divisions are printed from copper plates. They are distinguished by the names A and B in the sense already explained. The card B contains twenty columns, each 8 inches long, which if arranged in one line would form a logarithmic scale in duplicate of the length of 13 feet 4 inches, precisely similar to one of the scales on the common sliding-rule greatly magnified, and having a proportionately greater number of divisions. Card A has ten columns, each 16 inches long, and contains precisely the same matter as B, only differently arranged, as already explained. In using the cards, B is laid uppermost, in such a position that its columns alternate with those of A, the latter being visible through the openings or slits which are cut between the former. The divisions on A are on the right side of its columns, and those on B are on the left, extending to the edge of the slits, so that the divisions in those columns which work together are in close juxtaposition. In adjusting the cards, it will be found that a movement left or right to the extent of one column-breadth is equivalent to a movement of 8 inches up or down.

The largeness of the scale is such that, without undue crowding, the space from 1 to 1·1 is divided into a hundred parts; so that every number from 1000 up to 1100 has a division of its own, the last and nearest of these divisions being about  $\frac{1}{32}$  of an inch apart. On the best sliding-rules of the ordinary construction, this interval, which is here divided into 100, is only divided into 5. From 1100 to 2100 there is a division for every even number, from this point to 4800 a division for every fifth number, and thence to the end of the scale a division for every three-figure number.

Again, whereas in the ordinary rule only the *first* figure is printed, the first *three* figures are here printed as far as 479, and thence to the end of the scale the first *two* figures.

Some persons can never use the common sliding-rule success-

\* [The specimen in question was a copy of the "Universal Proportion-Table" published by Messrs. Longmans.—Eds. *Phil. Mag.*]



fully, on account of the difficulty of setting it with sufficient exactness, and of reading off correctly when the answer falls between two divisions. Such persons may content themselves with reading off from the *Proportion-Table* to the nearest division only, as the error thus involved averages considerably less than 1 part in a thousand. To produce so great an error as 1 per cent., there must be an error in setting or in reading off to the amount of fully  $\frac{1}{3}$  of an inch. In fact if all the divisions were erased and only the figures left, the instrument would still work as correctly as the ordinary slide-rule.

These considerations have not, however, operated as inducements to carelessness in the execution of the divisions. On the contrary, every effort has been made to carry accuracy to the utmost attainable degree. To this end the plates were first ruled with equidistant lines by means of a dividing-engine, the distance between the lines on plate B being equivalent to 1 in the third place of logarithms, and the distance between those on A one-tenth greater. Then, after proofs of these lines had been printed, and the principal divisions filled in with a pen to serve as a check against mistakes, the divisions were executed on the plates by means of the dividing-engine, the regulating wheel having fifty teeth, and each tooth corresponding to two in the fifth place of logarithms. The lines which had previously been ruled on the plates furnished a test of the equality of different parts of the screw; and the small inequalities, which were thus with the aid of a magnifying-glass detected, amounting in their greatest combined effects to three teeth of the regulating wheel, were in part corrected by advancing or retarding the wheel, the correction thus applied being generally less than the observed error, and never exceeding it; for it is obvious that the true correction would be in general about half the observed error.

It is considered certain that the distance of a division from its true place in no instance amounts to so much as  $2\frac{1}{2}$  teeth of the wheel, or 5 in the fifth place of logarithms, with the exception of the last two inches of the first column of B, where the divisions seem to be placed too high by something more than this amount, owing in part to an accident which occurred in this portion of the work, and in part to the fact that this column was the first executed, and that the corrections above mentioned were not applied until its completion. When great accuracy is required in the use of the *Proportion-Table*, this first column can always be dispensed with and the duplicate column (the eleventh) used in its stead, as plate B contains one column more than necessity requires.

A more serious source of error to be guarded against is unequal stretching or shrinking of the material on which the Table

is printed. It is not found that any serious difference exists between different parts of the same card; but it is found that some cards stretch or shrink more than others. This difficulty has thus far been completely overcome by selecting and pairing together those cards which agree best.

It is worthy of remark that the breaking up of the scale into parallel columns goes far to diminish the injurious effect of expansion or contraction; for in a straight slide-rule this cause operates on the whole length, whereas in the present arrangement it only operates upon a twentieth part of the length.

I may mention, as matter of curiosity, that in the case of a *circular* slide-rule it may be shown that, when expansion or contraction operates in one direction only and affects both circles alike, its injurious effect is, in the most unfavourable position, the same as if it operated tangentially along an arc equal to the diameter.

A somewhat singular property which incidentally attaches to the new arrangement is, that if any straight line be drawn across either of the two cards, the numbers through which it passes form a geometrical progression. Hence, if two numbers have an odd number of columns between them, a mean proportional can be found by observing where the joining line cuts the central intermediate column. As a particular case of this rule, the square root of any number can be extracted by taking a line from it to one or other of four fixed points, according to a simple rule which is of universal application.

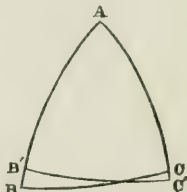
The accuracy of working by the *Proportion-Table* is practically found to be about the same as in the use of four-figure logarithms; that is to say, it may be depended on to about one part in four thousand; and it has the advantage of greater simplicity in use and less liability to mistake. To perform an operation in multiplication or division by logarithms, three references to Tables are required besides the addition or subtraction of the logarithms. In performing the same operation by the *Proportion-Table*, the arithmetical work of adding or subtracting is altogether dispensed with, and question and answer are read off at one view. The saving of labour is especially great when several numbers are to be multiplied or divided by the same factor, as one setting of the cards suffices for all.

The facility with which multiplication and division can thus be performed is of important service in simplifying certain trigonometrical processes. There are certain formulæ both in plane and spherical trigonometry which, though particularly simple and easily remembered, are not adapted to logarithmic computation, by reason of the number of references to the Tables which their use would involve. These formulæ are found to be conve-

niently available for use with the Proportion-Table. For example, when the sides of a spherical triangle are given, an angle can be found by the formula  $\cos A = \frac{\cos a - \cos b \cos c}{\sin b \sin c}$ , and that

with more ease and expedition than by the ordinary logarithmic methods. The hour-angle can thus be calculated from the observed altitude of sun or star; and if the calculation is carefully performed with the aid of a Table of natural sines carried to four places of decimals, the result will be correct to 1 or at most 2 minutes of arc—that is, to 4 or 8 seconds of time.

Another problem to which the Proportion-Table is well adapted is the clearing of lunar distances. Thus, if  $ABC$  be the spherical triangle formed by zenith, moon, and star, as observed, the sides of this triangle are known, and the cosines of the angles  $B$  and  $C$  at moon and star respectively can be calculated as above. Then, if accuracy be required, the correction  $\alpha$  of the observed distance can be computed from the corrections  $\beta$ ,  $\gamma$  of the apparent zenith-distances of moon and star respectively, by the formula



$$\alpha = \beta \cos B + \gamma \cos C + \left( \frac{\beta}{642} \right)^2 (1 - \cos^2 B) \cot a,$$

the small arcs  $\alpha$ ,  $\beta$ ,  $\gamma$  being expressed in seconds; and if the first term in this formula be worked to 4 figures, the second to 3, and the third to 2 figures, the result will be as correct as if 6-figure logarithms had been used in any of the ordinary methods. When no great accuracy is required, it suffices to use the first and second terms only, and to carry the work to only three figures. The average value of the third term is only  $4''$  or  $5''$ , and its sign is the same as that of  $\cot a$ ; so that it can be roughly allowed for without calculation.

The Proportion-Table is in fact sufficient and convenient for all the calculations which are usually made at sea; and its general use in navigation would go far towards enabling seamen to perform intelligently those processes which, from the very artificial form of the rules at present in use, they are now compelled to perform empirically. "Proportional logarithms," which, as at present used, are a source of perpetual mistakes even to expert computers (see note to Roper's 'Navigation,' p. 419), and have the effect of entirely concealing from a beginner every vestige of analogy in processes which are essentially identical, would no



longer be needed, as all cases of proportion could be easily worked in natural numbers.

It would not be difficult to construct, on the parallel-column principle, logarithmic scales of sines and tangents to be used with the *Proportion-Table*, in the same manner as Gunter's "lines of sines and tangents" are used with his "line of lines." But, on the ground of greater simplicity and intelligibility, it is considered better to dispense with these auxiliaries, and in their stead to use small *Tables* of natural sines and tangents.

While alluding to Gunter's scale, we cannot forbear quoting from Mackay's '*Description and Use of the Sliding Gunter in Navigation*' (2nd edit., 1812). He says in the preface, "Although a scale 2 feet long may be sufficient for performing any *day's work* with all the accuracy that may be desired, yet its divisions are too small for obtaining with exactness the apparent time from the altitude of a celestial object, the latitude from double altitudes and the elapsed time, or for reducing the apparent to the true distance; and therefore it is to be wished that its length was increased to at least double its present size." What would he have said to the present "*Table*," which instead of being only double is seven\* times the size of the old "*Gunter*."

We may add, by way of appendix, that we are at present trying the experiment of putting the *Proportion-Table* round a cylinder, the arrangement being so contrived that those divisions which work together will be in the same plane, and that the outer piece can be either rotated about the inner or moved longitudinally without rubbing the divisions. This plan promises some advantages, among others the abolition of the parallel lines which are now necessary for accurate adjustment; but we scarcely expect it will be found to admit of such rapid working as the present arrangement.

In concluding this paper, the author desires to express his obligations to Messrs. Fulton Brothers, engravers to calico-printers, Glasgow, for the valuable assistance which they afforded him in the mechanical execution of the *Table*, and for gratuitously allowing him the use, during a period of several weeks, of the very convenient and accurate dividing-engine with which the divisions were engraved.

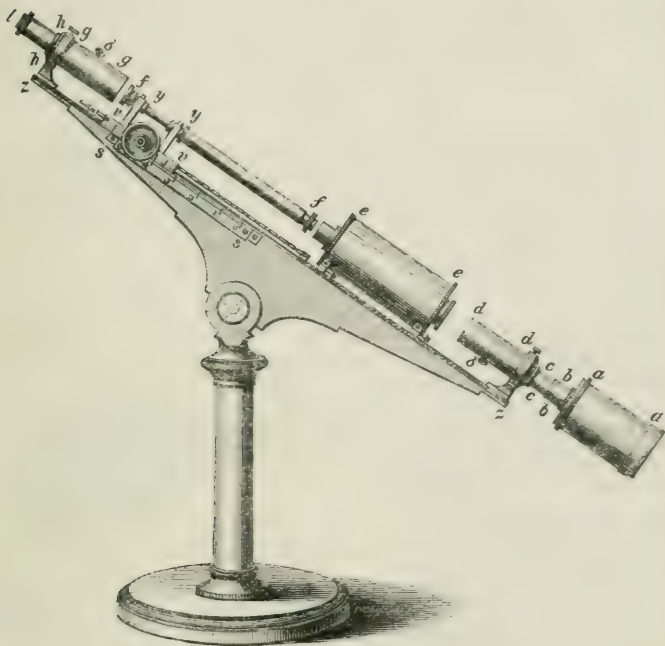
\* The real length of the so-called two-foot Gunter's scale is only 1 foot 10½ inches, after deducting margins.



XLVI. *On a new Optical Saccharometer.* By the Rev. JOHN H. JELLETT, M.A., Fellow of Trinity College, and Professor of Natural Philosophy in the University of Dublin\*.

THE instrument, of which the following is a description, is represented in the annexed woodcut, fig. 1. *aa* is a short tube, containing two large lenses, serving to condense the light

Fig. 1.

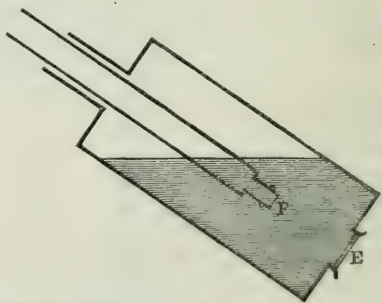


of a lamp, which is placed as nearly as possible in the principal focus of the lower lens. *bb, cc* is a short tube carrying at one extremity a lens, *cc*, and at the other extremity a diaphragm, *bb*, pierced at its centre by a very small hole which is situated in the principal focus of the lens *cc*, and also, when the instrument is adjusted, in the principal focus of the upper lens *a*. By this arrangement a beam of light is obtained emerging from *cc* sensibly parallel to the axis of the tubes. This beam is polarized by being transmitted through a Nicol's prism contained in the tube *dd*. *ee* is a vessel pierced at the lower end by a

\* Communicated by the Author, having been read before the Royal Irish Academy, January 26, 1863.

circular hole, which is closed with plate glass. This vessel contains a fluid possessing a rotative power opposite to that of the fluid under examination. This latter fluid is contained in the tube *ff*, which rests on the two upright pieces *yy*. These pieces are attached to the transverse piece *vv*, which carries a vernier whose divisions correspond to those of the scale *ss*, which is attached to the bar *zz*, which carries all the parts of the instrument. The transverse piece *vv* is capable of sliding along *zz*, this motion being produced by a chain attached at both ends to *zz*, passing round a spindle with a milled head, attached to *vv*. By these means a motion can be given to the tube *ff* parallel to its own axis; and by a very simple arrangement the zero of the vernier is made to coincide with the zero of the scale when the extremity, *f*, of the tube is in contact with the piece of glass covering the lower aperture in the vessel *ee*. It is plain, then, that the numbers read on the scale, which is graduated so as to be read to 0.001 inch, will denote the length of the column of fluid *EF* (fig. 2) interposed between the bottom of the vessel and the bottom of the tube. *gg* is an analyzing prism, constructed as before described\*. *hh* is a lens, and *l* a diaphragm with a small hole, at which the eye of the observer is placed. The polarizing and analyzing prisms are fixed in their places by small screws,  $\sigma$ ,  $\sigma$ , each passing through a transverse slit in the outer tube, so that when partly unscrewed they allow the prisms to turn through a small angle round the axis of the tube. In using the instrument, the polarizing prism may be set in any position, the analyzing prism being then carefully adjusted so that the tints in the two halves of the circular spectrum† may, when there is no fluid interposed, be exactly equal.

Fig. 2.



Suppose now that the object is to ascertain the strength of a given solution of cane-sugar. In this case the fluid to be used in the vessel *ee* may be French oil of turpentine. A certain quantity, the amount of which depends on the strength of the solution to be observed, having been poured into the vessel, the tube *ff* is then filled with a solution of sugar whose strength is accurately known. The tube is now replaced in the upright

\* Proceedings of the Royal Irish Academy, vol. vii. p. 348.

† Ibid. p. 349.

pieces, and the zero of the vernier made to coincide accurately with the zero of the scale. The milled head is now turned so as to draw back the tube until the tints on the two parts of the circular image seen through  $l$  become equal. The number on the scale corresponding to the zero of the vernier is then noted. Let this reading be  $R$ , and let  $S$  be the strength of the known solution.

Now, let this solution be removed from the tube, which is then to be filled with the solution whose strength is required. The same process having been gone through, let the new reading be  $R'$ ; then the strength required is given by the equation

$$S' = \frac{R'}{R} \cdot S.$$

If the experiment be carefully conducted, and if there be no error in the strength of the standard solution, the error in the measurement made as above described ought not to exceed 0.02 gr. per cubic inch for a single experiment. If the mean of a number of experiments be taken, the error will of course be still less\*.

The author has given to this instrument the name *saccharometer*, derived from one important use to which it may be applied. This, however, is but one of its applications; and there are many others at least as important. It may generally be defined to be an instrument by which the ratio of the rotatory power of any transparent fluid to that of a standard fluid may be accurately determined.

It is not desirable to use a very strong solution of the substance to be examined. The reason of this is the imperfect compensation which exists between fluids possessed of opposite rotatory powers. It is generally assumed that the ratio of the rotation produced in the planes of polarization of any two of the simple rays of which a white ray is composed is the same, whatever be the substance causing the rotation. It follows, indeed, from the law of Biot, that this is not accurately true; but it has been generally supposed that the error is too small to be perceived. If this were true, it would always be possible to assign to the lengths of two columns of oppositely rotating fluids such a ratio that the effect of the one should be accurately compensated by the effect of the other. But the author has found that in certain cases the error is very perceptible indeed. This is shown by the impossibility of giving to the tube  $ff$  any position

\* [Professor Jellett estimates the error to which even a practised experimenter is liable, in making a similar determination by means of Soleil's saccharometer, at not less than 0.5 grain of sugar per cubic inch of solution.]

in which the shades of colour are exactly the same in the two parts of the circular image. Suppose, for example, that the position of the tube is such that the plane of polarization of the mean ray has the same position as at first. This plane is then equally inclined to the planes of analyzation of the two parts of the analyzing prism. But this is not true of the planes of polarization of any of the other rays; of these, the less refrangible will have their planes of polarization nearer to one of the planes of analyzation, while those of the more refrangible are nearer to the other.

There will therefore be in the one half of the image a preponderance of red light, and in the other a preponderance of blue light, when the densities of the two parts are equal. The difference of colour, which makes it difficult to equalize these intensities with perfect accuracy, will evidently be greater the greater the amount of the rotations which the compensating fluids would severally produce, and therefore the greater the strength of the solution.

On the other hand, it must be remembered that the error in the result, arising from an incorrect position of the tube, is inversely proportional to the length of the column of the compensating fluid. Thus, if the reading of the scale be  $\cdot 1$ , an error of one division, or  $\cdot 001$ , will have the same effect on the result as an error ten times as great would have if the reading were  $1\cdot 000$ .

No general rule can be given for determining the strength of the solution which it is desirable to use. If the law of Biot, sc. that the amounts of rotation produced by the same substance in the planes of polarization of the different simple rays are proportional to the squares of the corresponding refractive indices, be strictly true, then, the more nearly these indices are in the same proportion for the fluid under examination and the compensating fluid, the stronger may be the solution used. If the fluid under examination be a saccharine solution, and the compensating fluid French oil of turpentine, a solution containing in each cubic inch thirty grains of sugar may be used without inconvenience\*.

\* The instrument here described was constructed by Messrs. Spencer and Son, of Aungier Street, Dublin, to whose ability, both in carrying out the instructions given to them, and in suggesting methods for overcoming practical difficulties, the author is much indebted.



XLVII. *On the Influence of the Tidal Wave on the Motion of the Moon.* By JAMES CROLL\*.

IN a paper "On the Influence of the Tidal Wave on the Motion of the Moon," which appeared in the Philosophical Magazine for August last, I inadvertently represented Professor William Thomson as having come to the conclusion that the earth, regarded as a time-keeper, is actually losing about four seconds in a year. This, however, is incorrect. In Professor Thomson's paper on the subject a certain state of circumstances as to the tides is specified, not as a probable hypothesis, but as one on which a superior limit of the amount of tidal influence on the earth's rotation may be estimated. On that hypothesis the earth would, one hundred years hence, be rotating so much slower than at present as to be then losing four seconds a year on a perfectly accurate chronometer regulated according to the earth's present rate.

In my two former papers on the influence of the tides, I endeavoured to show that the solar wave must exercise a retarding effect on the earth's motion round the common centre of gravity of the earth and moon, similar to what the lunar wave exercises upon the earth's rotation or motion round its own centre of gravity†. This, as was pointed out, follows as a direct consequence from the fact that, supposing the earth to have no rotation, still the waters of the ocean would have to rise and fall in order to maintain the solar wave, which in this case would move round the earth, not once in twenty-four hours as at present, but once in a month. And as this motion of the waters, slow as it no doubt would be, could not take place without heat being generated by friction and dissipated into space, the *vis viva* thus lost must be at the expense of the earth's motion round the common centre of gravity of the earth and moon; for, by supposition, there is no other motion from which it could be derived. It can be easily proved that this would tend to bring the earth nearer to the moon, and thus increase the moon's angular motion.

It has been shown by Professor William Thomson, and also by the Astronomer Royal, that, owing to the position of the tidal wave, the moon is drawn not exactly in the direction of the earth's centre of gravity, but a little to the east of that centre, and that in consequence of this, she is made to recede from the earth. Her orbit is enlarged, and her angular motion diminished.

It would therefore seem that the tides produce two distinct classes of effects, the one to a certain extent neutralizing the

\* Communicated by the Author.

† Phil. Mag. for April 1864 and August 1866.

other. The effect pointed out by Professor Thomson and the Astronomer Royal does not, however, in the least degree prevent the consumption of the *vis viva* of the earth's motion round the common centre of gravity, although to a certain extent, at least, it must prevent this consumption from diminishing the moon's distance and increasing her angular motion. But as this consumption of *vis viva* will go on throughout indefinite ages, if the present order of things remains unchanged, the earth and the moon must therefore ultimately come together.

XLVIII. *On the Locus of the Foci of the Conics which pass through four given Points.* By Professor CAYLEY, F.R.S.\*

THE curve which is the locus of the foci of the conics which pass through four given points is, as appears from a general theorem of M. Chasles, a sextic curve having a double point at each of the circular points at infinity; and Professor Sylvester, in his "Supplemental Note on the Analogues in Space to the Cartesian Ovals *in plano*" (Phil. Mag. May 1866), has further remarked that the lines (eight in all) joining the circular points at infinity with any one of the four points are all of them double tangents of the curve; whence each of these points is a focus (more accurately a quadruple focus) of the curve. It is to be added that, besides the circular points at infinity, the curve has 6 double points (3 of these are the centres of the quadrangles formed by the 4 points), in all 8 double points; the class is therefore = 14. Hence also the number of tangents to the curve from a circular point at infinity is = 10; viz. these are the 4 double tangents each reckoned twice, and 2 single tangents; and the theoretical number of foci is = 100; viz. we have

$$\begin{array}{lcl}
 16 \text{ quadruple foci or intersections of a double} & & \\
 \text{tangent by a double tangent . . . . .} & \left. \vphantom{\begin{array}{l} 16 \text{ quadruple foci} \\ 16 \text{ double foci} \\ 4 \text{ single foci} \end{array}} \right\} & 16 \times 4 = 64 \\
 16 \text{ double foci, or intersections of a double} & & \\
 \text{tangent by a single tangent . . . . .} & \left. \vphantom{\begin{array}{l} 16 \text{ double foci} \\ 4 \text{ single foci} \end{array}} \right\} & 16 \times 2 = 32 \\
 4 \text{ single foci, or intersections of a single tan-} & & \\
 \text{gent by a single tangent. . . . .} & \left. \vphantom{\begin{array}{l} 16 \text{ double foci} \\ 4 \text{ single foci} \end{array}} \right\} & 4 \times 1 = 4 \\
 & & 100
 \end{array}$$

To verify the foregoing results, consider any two given points I, J, and the series of conics which pass through four given points A, B, C, D; we have thus a curve the locus of the intersections of the tangents from I and the tangents from J to any conic of the series; which curve, if I, J are the circular points at

\* Communicated by the Author.

infinity, is the required curve of foci. Taking  $U + \lambda V = 0$  for the equation of a conic of the series, the pair of tangents from I is given by an equation of the form

$$(\lambda, 1)^2(x, y, z)^2 = 0,$$

and the pair of tangents from J by an equation of the like form

$$(\lambda, 1)^2(x, y, z)^2 = 0;$$

and by eliminating  $\lambda$  from these equations, we obtain the equation of the required curve. This in the first instance presents itself as an equation of the eighth order; but it is to be observed that in the series of conics there are two conics each of them touching the line IJ, and that, considering the tangents drawn to either of these conics, the line IJ presents itself as part of the locus; that is, the line IJ twice repeated is part of the locus; and the residual curve is thus of the order  $8 - 2 = 6$ ; that is, the required curve is of the order 6. The consideration of the same two conics shows that each of the points I, J is a double point on the locus. Moreover, by taking for the conic any one of the line-pairs through the four points, it appears that each of the points (AB.CD), (AC.BD), (AD.BC) is a double point on the curve: this establishes the existence of five double points. The two conics of the series which touch the line IA are a single conic taken twice, and the consideration of this conic shows that the line IA is a double tangent to the curve; similarly each of the eight lines I(A, B, C, D) and J(A, B, C, D) is a double tangent to the curve. Instead of seeking to establish directly the existence of the remaining three double points, the easier course is to show that, besides the four double tangents from I, the number of tangents from I to the curve is  $= 2$ ; for, this being so, the total number of tangents from I to the curve will be  $(2 \times 4 + 2) = 10$ ; that is, I being a double point, the class of the curve is  $= 14$ ; and assuming that the depression  $(6.5 - 14) = 16$  in the class of the curve is caused by double points, the number of double points will be  $= 8$ . But observing that in the series of conics there is one conic which passes through J, so that the tangents from J to this conic are the tangent at J twice repeated, then it is easy to see that the tangents from I to this conic, at the points where they meet the tangent at J, touch the required curve, and that these two tangents are in fact (besides the double tangents) the only tangents from I to the curve; that is, the number of tangents from I to the curve is  $= 2$ .

Considering I, J as the circular points at infinity, and writing A, B, C, D to denote the squared distances of a point P from the four points A, B, C, D respectively, then, as remarked by Pro-

fessor Sylvester, the equation

$$\lambda\sqrt{A} + \mu\sqrt{B} + \nu\sqrt{C} + \pi\sqrt{D} = 0$$

(where  $\lambda, \mu, \nu, \pi$  are constants) is in general a curve of the order 8; but the ratios  $\lambda:\mu:\nu:\pi$  may be so determined that the order of the curve in question shall be  $= 6$ ; the resulting curve of the order 6 is (not one of a group of curves, but the very curve) the locus of the foci of the conics through the four points. And the determination of the ratios  $\lambda:\mu:\nu:\pi$  is in fact quite simple; for writing

$$\begin{aligned} A &= (x-a)^2 + (y-a_1)^2 \\ &= \rho^2 - 2(ax + a_1y) + \&c. \\ &\quad (\text{if } \rho^2 = x^2 + y^2), \end{aligned}$$

and therefore

$$\sqrt{A} = \rho - \frac{ax + a_1y}{\rho} + \&c.,$$

with similar values for  $\sqrt{B}$ ,  $\sqrt{C}$ ,  $\sqrt{D}$ , it is easy to see that, considering  $\lambda, \mu, \nu, \pi$  as standing for  $\pm\lambda, \pm\mu, \pm\nu, \pm\pi$  respectively, the conditions for the reduction to the order 6 are

$$\begin{aligned} \lambda + \mu + \nu + \pi &= 0, \\ \lambda a + \mu b + \nu c + \pi d &= 0, \\ \lambda a_1 + \mu b_1 + \nu c_1 + \pi d_1 &= 0, \end{aligned}$$

and hence that the required equation of the curve of foci is

$$\Sigma \left\{ \begin{vmatrix} 1, & 1, & 1 \\ b, & c, & d \\ b_1, & c_1, & d_1 \end{vmatrix} \sqrt{(x-a)^2 + (y-a_1)^2} \right\} = 0,$$

or, as this may also be written,

$$\Sigma \pm (B, C, D) \sqrt{A} = 0,$$

where  $(B, C, D)$ , &c. are the areas of the triangles  $B, C, D$ , &c.

I remark, in conclusion, that the number of conditions to be satisfied in order that a curve may have for double points two given points  $I, J$ , may have besides six double points, and may have for double tangents eight given lines, is  $(3 + 3 + 6 + 16 =) 28$ ; the number of constants contained in the general equation of the order 6 is  $= 27$ . The conditions that a curve of the order 6 shall have for double points two given points  $I, J$ , shall besides have six double points, and shall have for double tangents four given lines through  $I$  and four given lines through  $J$ , are more than sufficient for the determination of the sextic curve; and the existence of a sextic curve satisfying these conditions is therefore a theorem.



In the case where the points I, J lie on a conic of the series, the consideration of this conic shows that the curve has a ninth double point, the pole of the line IJ in regard to the conic in question: in this case the sextic curve, as is known, breaks up into two cubic curves.

P.S. In general the curve  $\lambda\sqrt{A} + \mu\sqrt{B} + \nu\sqrt{C} + \pi\sqrt{D} = 0$  has (exclusively of multiple points at infinity) six double points; viz. these are situate at the intersections of the pairs of circles,

$$(\lambda\sqrt{A} + \mu\sqrt{B} = 0, \quad \nu\sqrt{C} + \pi\sqrt{D} = 0),$$

$$(\lambda\sqrt{A} + \nu\sqrt{C} = 0, \quad \mu\sqrt{B} + \pi\sqrt{D} = 0),$$

$$(\lambda\sqrt{A} + \pi\sqrt{D} = 0, \quad \mu\sqrt{B} + \nu\sqrt{C} = 0).$$

In the case of the curve of foci, the first, second, and third pairs of circles intersect respectively in the points (AB.CD), (AC.BD), (AD.BC), which, as mentioned above, are double points on the curve; and they besides intersect in three other points, which are the other three double points mentioned above.

Professor Sylvester reminds me that he mentioned to me in conversation that he had himself obtained the foregoing equation  $\Sigma \pm (B, C, D)\sqrt{A} = 0$ , for the locus of the foci of the conics which pass through the four points A, B, C, D.

Cambridge, October 10, 1866.

## XLIX. *Affinity and Heat*.

By H. SAINTE-CLAIRE DEVILLE\*.

ALL the labours, all the tendencies of modern science lead to the identification of the forces which come into play in the physical and chemical phenomena of nature; all the numerical determinations which have been obtained tend to establish their equivalence in the most rigorous manner. Affinity and cohesion cannot escape this identification, and already the mechanical theory encloses them within the circle of reasonings which must soon dispel whatever vague and mysterious notions may still be connected with them.

It cannot be concealed that the study of primary causes, in the phenomena which we observe and measure, presents in itself a serious danger. In the absence of any precise and independent definition of special facts, the consideration of primary causes leads us, oftener than we suppose, into really begging the ques-

\* Translated from the first chapter of a series of Lectures on "Dissociation," published in the *Lçons de Chimie* for 1864-65.

tion and contenting ourselves with specious explanations which cannot stand a severe criticism. Affinity especially, defined as the *force* which determines chemical combinations, has been for some time and still is an occult cause, a sort of *archée* to which are referred all facts which are not understood, and which thenceforth are considered to be explained, whereas they are only classed, and often badly classed. Thus to the catalytic force\* are attributed a host of phenomena which are very obscure, and will remain so, I imagine, if they are referred in the lump to an entirely unknown cause. It was certainly supposed that they belonged to the same category when the same name was given to them. But the legitimacy of this classification even has not been demonstrated. What can be more arbitrary than to class together the catalytic phenomena which depend on the action, or on the *presence* of spongy platinum or of concentrated sulphuric acid when the platinum and the acid, so to say, take no part in the action? These phenomena may perhaps be hereafter explained in an essentially different manner, according as they have been produced under the influence of an eminently porous substance like spongy platinum, or under the influence of a very energetic chemical agent like sulphuric acid.

Hence in our investigations we must omit all those unknown forces to which recourse has been had only because their effects have not been measured. On the other hand, all our attention ought to be fixed on the observation and numerical determination of those effects, which alone are within our reach. By this work their differences and analogies are established, and new light results from these comparisons and these measurements.

Thus heat and affinity are constantly concerned in our chemical theories. Affinity eludes us entirely; yet we attribute to it the combination which is the effect of this unknown cause. Let us then investigate merely the physical circumstances which accompany combination, and we shall see how many curious approximations, how many measurable phenomena, present themselves to us at every moment. Heat, they say, destroys affinity; let us, then, persistently investigate the decomposition of bodies under the influence of heat estimated in quantity or work, in temperature or *vis viva*; we shall at once see how fruitful is this study, and how independent of hypothesis, of any unknown force, unknown even from the point of view of the kind of unit to which its exact or approximate measure is to be referred. It is in this sense especially that affinity, regarded as a *force*, is an

\* This applies to the forces recently invented—force of diffusion, force of solution, crystallogenic force, and all special attractive and repulsive forces which are brought in to explain the phenomena of calefaction, superfusion, electrical phenomena. &c.

unknown cause, at least when it is not merely the expression of a quality of matter; in this case it should merely serve to designate the fact that such and such substances can or cannot combine under certain well-defined conditions.

One point is very urgent; that is, to define combination itself. Seeking attentively the state of our knowledge in this respect, I find, in the first place, that the definition of *combination* must comprehend *solution*, and can only exclude mixture. In fact the phenomena of solution and of combination are joined by a continuous chain which it is impossible to break at any one point. Every one knows that interminable discussions have been raised on this subject,—for instance, in respect to metallic alloys and their liquation; in reference to salts, acids, energetic bases, and their action upon water, alcohol, &c. The most certain conclusion which can be drawn is, that there are all possible intermediate stages between the phenomena of combination and the best-characterized phenomena of solution.

In endeavouring to formulate in the clearest manner the ideas now current on combination, I find it cannot be better defined than by the fact of *change of state*. When two substances put in presence change condition, they combine. This change of condition, defined in the ordinary manner, shows itself by some new property, whether physical or chemical, which discloses new qualities of the combined substances—qualities, whether physical or chemical, which distinguish the combination from simple mixture. I will give an example.

The question has been asked, Is air a mixture or a combination? How has this question been solved? The physical and chemical properties of the elements of air (oxygen and nitrogen) and of air itself have been successively studied. They have been found to be identically the same, always equal in the case of air to the mean of these properties determined upon each element singly. Hence it has been concluded that nitrogen and oxygen, coming into contact under ordinary atmospheric conditions, exert no appreciable action on one another, that, therefore, the condition of the gas has undergone no change—that, in short, air is a mixture and not a combination of nitrogen and oxygen.

It must be observed that recourse has always been had successively to the physical properties of air to solve so important a question. Biot went so far even as to adduce the equality between the refractive indices of air and of the mean of the indices of oxygen and of nitrogen as a proof in favour of the opinion now generally admitted. If, in fact, there had been found in a constant manner a measurable physical property, different in air and in a mixture of oxygen and nitrogen, the conclusion would have been immediately drawn that air was a combination. There



would have been a change of condition, owing to the mixture of the two gases; and the beautiful verification of Lavoisier would have been invalidated in an irrefutable manner. The argument drawn from the proportions of the two gases, oxygen and nitrogen, which are not in atomic proportion in the air, is without value. One of the two elements might simply have been in excess over a combination of the two others. There would have been mixture and combination, and therefore change of state for one portion of the air alone, which is not the case.

Combination being thus characterized by change of state, and therefore well defined; what is the particular form of combination which merits more especially the name of solution? I say especially; for it would be impossible to say now whether water and sulphuric acid, acetic acid, chloride of calcium, and many other bodies are combined with or merely dissolved in one another. But there is a fundamental difference between the *effects* produced when potash is thrown into sulphuric acid, and the effects observed when common salt is placed in water.

In both cases the change of state is manifest; but when sulphate of potash has been obtained after the *combination* of sulphuric acid and of potash, new chemical properties have become strikingly evident. It is in fact by these chemical properties that change of state is most clearly manifested at the time of energetic combination. In the second place, when the *solution* of common salt in water is effected, the chemical properties of the elements in presence remain virtually unchanged. First a true fusion of the salt is noticed, which assumes the liquid state—a change of physical condition accompanied most frequently by an absorption and disappearance of heat,—then variation in the density, or phenomena of contraction\*, alteration in the volume of the elements, which, again, is a change of physical properties which essentially characterizes true *solution*.

Yet an exclusive value must not be given to these differences, in the chemical properties to designate a combination, in the physical properties to designate a solution. We all know, from the beautiful experiments of Henry Rose, that very weak solutions of the alkaline carbonates of borax have reactions differing essentially from those which their concentrated solutions present. This remark is sufficient once more to show that the phenomena due to changes of state cannot be ranged in two distinct categories, combination and solution. I shall recur to this once more, in reference to diffusion, or the indefinite extension of matter in menstrua.

What I have said enables me to use the two words, combination and solution, in a perfectly definite sense, without the risk of considering them to express an unknown cause, and cha-

\* *Contraction* is here a generic term; if it be negative, it is an expansion.



acterizing them simply by the effects which are manifested in our daily chemical operations. I hope, therefore, to be logical in the following reasonings.

When two gases are mixed which spread uniformly into one another, can the phenomenon of what is called their *diffusion* be compared to the solution of two liquids in one another? I do not think so.

Suppose we place together bisulphide of carbon and white phosphorus at a temperature convenient for the melting of the phosphorus, oil and sulphuric ether, chloride of calcium dissolved, acetic acid and water; we might obtain very decided changes of physical condition, characterized principally by an elevation or depression of temperature, and by a change of density: in a word, the physical properties of these solutions might vary without the chemical properties being sensibly modified.

Is this the same with gases? Experiment shows us, first of all, that gases frequently combine without apparent absorption or disengagement of heat (oxide of carbon and chlorine, chlorine and hydrogen in diffused light). But whenever this disengagement of heat can be confirmed, the chemical properties have been profoundly changed. Moreover Gay-Lussac's law proves that gases which contract in combining do not change in volume in the same way as liquids which dissolve. The volume of the combination is always a simple fraction, and often a very small one, of the volume of the elements of this combination. Thus contraction, when it exists, not merely characterizes the combination of the gases, but allows the composition to be deduced therefrom.

Nothing of the same kind can be remarked in the solution of liquids, where the contractions follow no simple law, and do not enable us to foresee any change in the chemical properties of the elements which interpenetrate by solution; further, the thermal phenomena which may be manifested at the moment in which the liquids interpenetrate do not necessarily imply change of their chemical properties.

Observing that the physical and chemical properties of bodies cannot be separated in a more absolute manner than can the phenomena of combination and of solution, we conclude, first, that the diffusion of gases is essentially different from the solution of liquids, and therefore that whenever, from the mixture of two gases, there results a calorific phenomenon, there is change of condition, and therefore combination.

The phenomena observed on the contact of liquids and solids which mutually dissolve each other are far more complex, and deserve a special analysis.

In attacking this question experimentally a large number of

the physical properties of bodies must be known, and therefore be determined whenever they are unknown. Hence all the complications which would be a source of trouble in calculating the effects observed (for instance, the latent heat of the fusion of solids) must be removed at the outset in this investigation. Hence my researches have hitherto been limited to the determination of the calorific phenomena manifested on the contact of liquids which combine or dissolve and produce a liquid.

In general, two bodies which dissolve, contract. I shall begin by defining what I call heat of contraction, either in the particular case of liquids or in the general case.

Suppose we take a body whose weight is unity: knowing the law of its expansion as a function of the temperature, we can calculate the temperature at which this body would lose a given fraction of its volume; and knowing the specific heat of this body within the limits of experiment, we can calculate the heat of contraction corresponding to this diminution of volume. Hence we can obtain the quantity of heat necessary for a given variation of the density. That will be the heat of contraction.

Suppose we take water and sulphuric acid at  $0^{\circ}$  superposed in a spherical flask provided with a perfectly cylindrical narrow neck; suppose that the two surfaces of contact are separated by an obstacle easy to break, such, for instance, as a spider's web; and suppose, further, that the vessel is athermanous, and can neither be heated nor cooled—in other words, that its specific heat is zero.

The level of the upper of the two liquids being at A, they are mixed in an infinitely short time, and in a complete manner. Heat at once manifests itself, and assumes a maximum value, which is indicated by a thermometer (whose weight can be neglected) placed in the interior of the liquid; this temperature will be  $t$  degrees.

At the same moment, the temperature being supposed to be equal and invariable, the liquid will sink in the narrow neck to the level B. Finally, cooling the acid to its original temperature of  $0^{\circ}$ , its volume will again diminish until the surface is level with the point C. The volume of the cylindrical space AC divided by the original volume of the elements (water and acid), which I shall call V, will represent the contraction. Calling  $v$  the volume of the acid after mixture, we shall have for this contraction the value\*

$$1 - \frac{a}{V}.$$

What I call heat of contraction is the quantity of heat necessary to restore the volume of the mixture  $v$  to the volume V. Know-

\* S being the section of the cylinder, we have  $V - v = AC \times S$ .

ing the coefficient of expansion  $k$  of the liquid from  $0^\circ$  to a temperature a little higher than  $\theta$ , the specific heat  $c$  of the liquid being supposed constant between the same temperatures, and  $m$  its weight, we shall have for the heat of contraction  $Q$  the value

$$\left(\frac{V}{v} - 1\right) \frac{m}{k} = Q,$$

the temperature  $\theta$ , at which the mixture resumes its original volume, being

$$\left(\frac{V}{v} - 1\right) \frac{1}{k} = \theta.$$

I have determined, by methods which I cannot describe here, the heats of contraction of a great number of liquids resulting from the combination or the solution of two elements also liquid, such as sulphuric acid and water in very variable atomic proportions, sulphuric acid and soda of various degrees of dilution, water and alcohol, water and acetic acid, water and formic acid, varying the proportions, which are always atomic, in a great number of modes\*.

The following is the result of my experiments:—

(1) When two liquids combine or dissolve and give a product which is also liquid, the highest temperature resulting from the mixture is generally smaller than the temperature  $\theta$  which contraction could give if the liquid disengaged all the heat corresponding to this contraction.

(2) Hence the quantity of heat disengaged in these kinds of combinations or solutions is always less than the heat of contraction.

It follows that, in all the cases which I adduce, the mere phenomenon of contraction is sufficient, and more than sufficient, to explain the development of heat in chemical combinations. Hence part of the heat which contraction disengages becomes latent in the new compound, and there plays an important part which I shall afterwards point out†.

This quantity of heat, which is latent or lost to the thermo-

\* Compare *Comptes Rendus*, vol. 1. pp. 354 & 584.

† The heat absorbed has served to reduce the liquid from the original volume corresponding to the level A and the temperature  $\theta$ , to the volume corresponding to the level B and the temperature  $t$ ; it is indicated by the temperature  $\theta - t$ . The original liquid has therefore been forced upon itself, owing to combination. Knowing its coefficient of compressibility between  $\theta$  and  $t$ , and its specific heat  $C$  between these temperatures, its mass being  $m$ , we might calculate the weight  $P$  with which the liquid at A must be charged to make it sink, on being compressed, to the level B. The number of kilogrammetres obtained on multiplying this weight by the distance AB would correspond to the work of a quantity of heat equal to  $(\theta - t)mC$ , and would enable us to obtain the mechanical equivalent by a chemical method



meter, may be expressed by a very simple fraction of the heat of contraction, if we assume that the specific heat is invariable between the temperature 0 and  $\theta$ , which is never the case unless  $\theta$  is very small. On this hypothesis it becomes

$$1 - \frac{t}{\theta} = \pi.$$

Considering one and the same liquid, we may, in consequence of the errors introduced by delicate and numerous determinations, suppose the temperatures to be proportional to the *vires viva*, or to the square of the velocities in the molecules the movement of which produces heat. The number  $\pi$  represents, then, the fraction of this *vis viva* which has not been expended at the moment of the combination or of the solution. It is, if we like, the fraction of the heat of contraction which has remained latent in the product of the reaction, and  $\pi$  is positive.

In the experiments I have terminated I have only found one single exception; and that is in the case of the formation of sulphate of soda by means of two dilute solutions, one of sulphuric acid and the other of caustic soda. Sulphate of soda expands at the moment of its formation, and  $t$  is greater than  $\theta$ , so that  $\pi$  becomes negative, which is a nice point to explain. But the study of the phenomena of saturation in these solutions will, I hope, enable me to explain this abnormal phenomenon, like the contraction of water by heat, or the expansion of bismuth at the moment of its solidification, &c.\*

The contraction observed on mixing with water monohydrated acetic acid or saline solutions is considerable, and the cooling of the combination or solution very noteworthy, as had already been observed by Rudberg, if I am not mistaken. In that case  $t$  becomes negative, and  $\pi$  is greater than unity. Thus at the moment of the reaction the product at first renders latent all the

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which appears worthy of attention. In order that these temperatures may be exact, not merely the variations of the specific heat  $C$  between  $\theta$  and  $t$  must be known, which is determined by the ordinary methods, but also its variations for pressures comprised between 1.033 kil. and  $\frac{P}{S}$ ,  $S$  being the section of the cylinder AB. It will be conceived that this second class of variations might be determined by observing the velocity of cooling of liquids placed in thermometer-tubes closed successively at the ordinary pressure and the pressure  $\frac{P}{S}$ .

Under these conditions the mechanical equivalent would be obtained by replacing the compression of gases by the compression of liquids; the mechanical agent would be simply replaced by the chemical action.

\* Since writing these lines, M. J. Regnauld has made observations on this subject which lead to a system of explanation far superior to my own. (*Journal de Pharmacie*, 4 sér. vol. i. p. 401.)



heat of contraction, which is very great, and then some sensible heat taken from itself and from the adjacent bodies. MM. Bussy and Buignet have recently observed the same fact and others of the same kind, especially in the mixture of hydrocyanic acid and water.

It is very probable that the preceding considerations would apply to solid bodies, if we knew their latent heat of fusion, to calculate formulæ which give the heat of contraction.

When a solid dissolves in water, it first absorbs the quantity of heat necessary to melt it, then a certain quantity of heat which increases with the proportion of the solvent, and which corresponds to the extension of the body dissolved in its menstruum. These facts, which are of great importance, were determined in the most rigorous manner by M. Person, and deduced from observations made more especially on nitrate of potash. To these thermal units, expended in the work of solution, must be added the heat of contraction absorbed and determined by the methods I have described.

Thus the more a soluble substance is diffused in its solvent, the more heat it has absorbed, which it has borrowed either at the contraction (which appeared indefinite) in the act of solution, or from the adjacent bodies when there is cooling during solution and extension. Thus, though I use an expression paradoxical in form, it may be affirmed that every body which cools while it undergoes molecular modification, is really heated, by borrowing heat from the adjacent bodies, and from itself first of all. The latent heat which it possesses is increased to the extent of all the heat which has disappeared either by the fact of spontaneous cooling or by diminution of the heat of contraction. It is, in fact, so much heat lost, and therefore changed into motion of the molecules, or, if we like, into affinity, if we thus designate the force which produces this motion.

All this heat, lost apparently, will reappear completely when the solution is made to undergo the phenomenon the inverse of extension, that is to say, concentration. Hence, in the cycle comprehending the solution of a salt at the ordinary temperature and its crystallization by spontaneous evaporation (supposing the salt to be anhydrous like nitrate of potash), all the quantities of heat borrowed from without, and from the contraction during the period of solution and of extension, will reappear and be given out during concentration and crystallization. Hence it might be said that these solutions contain (and that will only be true potentially) all the heat which water and the salt have absorbed during the development of the phenomenon.

Thus a body which cools spontaneously does really become heated by all the latent heat which its molecules fix; and it may

be conceived that in an almost indefinite state of extension it might even be decomposed by the heat which it has absorbed at each addition of the solvent. In this manner is to be explained the decomposition by diffusion produced by Mr. Graham, and which serves as the basis of his admirable method of dialysis.

If you put bisulphate of potash in the internal diffusion-vessel (two cylindrical concentric vessels, Graham's first apparatus), you know that the illustrious physicist shows you sulphuric acid separating from neutral sulphate of potash and passing into the external vessel.

There we have a true decomposition which is necessarily accompanied by the absorption of a certain quantity of heat. Let us inquire to what it is due. If we add sulphuric acid to sulphate of potash, both in dilute solution, the liquid will become heated; but the quantity of heat thus produced will always be less than the heat of contraction calculated in the manner I have shown. In fact there will be a transformation of the heat which should have become sensible during the contraction, into latent heat; and when this has become considerable enough, decomposition by diffusion will take place.

In order that the inverse of the original effect may take place, the combination which is destroyed must take up the quantity of heat which became sensible at the time it was effected. It is the latent heat stored up during solution which furnishes it; but it is inadequate for completely producing this effect, and thus the phenomenon is only partial, as Mr. Graham has well observed.

The phenomena of decomposition by diffusion take place therefore in a continuous manner, like the decomposition of gases by heat, and all that I am about to say respecting dissociation and its tension (which might here be replaced by the ratios of weights) is absolutely applicable to them.

Whether diffusion takes place in two concentric vessels as I have supposed, or in Graham's new membrane apparatus, the process is the same.

Suppose that a body with little stability, such as hydrochlorate of alumina, a body which is reduced to its elements by the least heat, be introduced into the dialyzer, above the membrane or parchment-paper which serves as a filter with very close meshes. Below this filter is water, which I assume to be constantly pure.

The hydrochlorate of alumina absorbs the more heat the greater the quantity of water in which it is dissolved, so that at a given moment it may be supposed to contain so much heat that if this heat became sensible and were applied to its elements they would at once separate. At this moment hydrochloric acid becomes free, and hydrated alumina separates in particles extremely divided, which occupy all the liquid in which the sepa-

ration is effected. Hence it ought to have all the properties of a dissolved substance. It will soon be seen that these properties are only apparent.

That is what takes place in the dialyzer; moreover the hydrochloric acid passes through the filter, and alumina remains on the surface in the state of apparent solution—or in the colloidal state, to use the expression which Mr. Graham has adopted. Yet in practice this reaction does not take place exactly in this manner.

We may suppose the permeable membrane divided into two horizontal layers,—one the higher layer, where the hydrochlorate of alumina penetrates (this has little thickness), the other the lower layer, where water alone penetrates. It is clear that in an apparatus of this kind the solution of hydrochlorate of alumina will very soon find a layer near the surface where the water, which is renewed with rapidity, will be in considerable proportion as compared with hydrochlorate. In this layer the decomposition of the salt will then take place by indefinite diffusion (consequently by the effect of heat), the hydrated alumina will remain in the state of colloidal particles on the upper surface, and the hydrochloric acid will be carried away by the water. The colloidal layer thus produced will itself become a true filter, and the phenomena of decomposition may go on in its interior.

Yet decomposition by diffusion cannot be complete; for it varies with the ratio of the quantity of water put in contact with hydrochlorate of alumina, and with the quantity of hydrochloric acid which this water contains. In other words, the quantity of water separated by diffusion will be the smaller the more this water is charged with hydrochloric acid (this acid arising from a portion of hydrochlorate already decomposed). Everything takes place as if the heat necessary for entirely decomposing hydrochlorate of alumina could never be entirely equal to that which extension furnishes to its molecules, within the limits of our experiments.

Thus the phenomenon of dialysis is never complete; a little hydrochlorate of alumina always passes through the membrane, and the colloids cannot be separated in an absolute manner by means of diffusion.

This principle has numerous applications. If we admit generally that all solutions are cooled on being diluted, as is shown by a great number of experiments—if, moreover, we assume, as my experiments seem to show, that in every change of state accompanying solution there is a loss of *vis viva*, and hence a concentration of latent heat in the substances dissolved, and in their menstrea, we can understand a great number of phenomena the explanation of which escapes us, and bring them within the class of known phenomena.

Thus the sap of trees is, so to say, pure water at the moment



it begins to move, and contributes to the increase of the plant. It is a solution so diluted with carbonic acid and organic or mineral substances drawn from the seed or from the soil, that its molecules may be considered absolutely free, or separated by the latent heat which is there accumulated. When this solution reaches the parenchyma of the leaves, where both its concentration and its alteration on contact with the elements of the air take place, it may be said that all molecular equilibria are successively possible; and if circulation raises them to concentration or to combination at a given moment, all the elements of carbonic acid, of water, and of the mineral principles which the sap contains may group themselves according to a formula determined previously by the rapidity of the circulation, the nature of the leaves, and the physical circumstances necessary for the life of the plant. In this manner we can probably account for the diversity which the act of vegetation imprints on the nature of the products it forms with the elements of water, of carbonic acid, of ammonia, and of some minerals.

It is also in the heat stored up by solution that we must seek the principal element of the decomposition by vegetables of carbonic acid into carbon and oxygen—a phenomenon regarding which we must confess our total ignorance.

A most remarkable experiment which M. Berthelot has made, by placing together carbonic oxide, water, and potash, belongs to actions of this kind.

Carbonic oxide dissolves in potash, and absorbs during its extension\* in the liquid a certain number of thermal units beyond that which the loss of *vis viva* by contraction doubtless allows it to retain at the moment of its liquefaction. This solution, which takes place in very small quantity at a time, owing to the slight solubility of the gas, is really a considerable extension, which, thanks to dissociation by diffusion, gives to the molecules of carbonic oxide the heat necessary for entering into direct combination with the elements of potash. In this reaction (it is moreover effected with the slowness which characterizes all operations where solution is necessary when the solubility is small) the heat is fixed which formic acid needs for its existence. It is the origin of this heat taken from the solution by a combination effected between bodies in the *nascent* state, and which will be disengaged in the form of sensible heat when formic acid is decomposed by spongy platinum, as has been done by Berthelot, or when formic acid is burned, as was done by Favre and Silbermann some time ago.

\* A given weight of carbonic oxide has a far less density in its aqueous solution than in the atmosphere formed by the gas itself on the surface of the solvent.



Combination is almost always produced by the destruction of motion, sometimes by the transformation of heat into motion. In the first case there is a disengagement of heat, in the second a cooling or absorption of heat. In the second category are to be included all those bodies which I have proposed to call explosive, that is, which render into sensible heat the motion they have acquired in absorbing latent heat. Formic acid, a great number of organic compounds, as well as the explosive compounds of nitrogen, are in the latter category; and these are rarely produced by the direct union of the elements, but are obtained by the interchange of their elements in the body of more or less dilute solutions. It is assumed that then the molecules are in contact in the nascent state. Here we must be on our guard; this term still includes the idea of an occult cause. It must be employed with extreme reserve; and by it must be understood a system of circumstances in which the molecules may change their state of equilibrium on finding about them latent heat or, in general, the causes of motion necessary for producing and exciting this change of state. The origin of the expression which renders this idea implies an hypothesis which may give rise to a vicious circle in the minds of young chemists, or of persons who have not maturely reflected on these definitions. It is seen, from the explanations which I have given, that a more or less dilute solution really contains a certain quantity of heat, arising either from gain by contraction, or by cooling by expansion. Hence most of the combinations which are due to the nascent state ought to take place in solutions—especially those which take place under cooling—those which give explosive substances\*.

From what has been adduced in this chapter, it will be seen how great in their origin are the differences between the calorific effects produced when gases combine with each other, and the calorific effects developed by the combination or solution of liquids with each other. In the latter case the heat of contraction has almost always been sufficient, and more than sufficient, to account for all. As to gases, this heat of contraction, which may be calculated by formulæ given above, is always very small as compared with the heat disengaged during combination; it may, indeed, be zero, as in the case of hydrogen and chlorine, and, indeed, whenever gases combine in equal volumes, and hence without condensation. Therefore we must admit that gases contain of themselves, and in the latent state, the principle of motion or of heat which is manifested at the moment of combination.

\* I call in general those bodies explosive which at the moment of their decomposition contain more heat than the bodies into which they are reduced require to exist in the condition of simple substances.

Lavoisier considered oxygen to be composed of a certain unknown radical and of this principle, which he materialized under the name caloric. This point of view I shall develope in a following chapter.

In direct combinations the motion is destroyed and converted into heat: just as a finite velocity can only be imparted to a body in a finite time, so combination will always require for its production a greater or less time, but always a definite one.

As the phenomena of indirect combination (or that produced by the nascent state) require (1) a solution, (2) an absorption of heat or a cooling, the time necessary for their development will be greater (1) as the solubility of the substances acting in the menstrua is smaller, (2) as the absorption of heat is greater.

The action of time need not be mysterious; we must always either explain it simply, or wait for facts to account for it.

L. *On the Dynamical Theory of Electricity.*

By C. BROOKE, F.R.S.

To Professor Tyndall, F.R.S.

16 Fitzroy Square, W.

October 13, 1866.

MY DEAR SIR,

I HAVE lately been led, in relation to a new edition of my 'Elements of Natural Philosophy' now in the press, to reconsider the whole question of electricity, and I have become strongly impressed with the reality of the dynamical theory. I have hence naturally been induced to look about for confirmatory facts; and a strong, and (to the best of my knowledge and belief) a new fact has presented itself to me. It has long been known that if a bar of antimony and one of bismuth be connected, and a current be transmitted from antimony to bismuth, heat will be developed at the point of junction; and, on the contrary, if the current pass from bismuth to antimony, cold will be produced. Now it struck me that if in the former, as in all other cases in which heat is developed in the passage of a current, a portion of *electric potential* is (as I believe) converted into *thermic potential*, or heat, there ought in the latter case to be an inductive conversion of thermic into electric potential; and if so, there should be a *loss* of current in the first instance, and a *gain* in the second: and such appears to be the fact. On duly balancing the thermoclement above mentioned in a Wheatstone's bridge, the deflection of the needle followed the direction of the current, and the anticipated loss or gain of current was fully realized. If you can find room for this notice in the Philosophical Magazine, you will greatly oblige,

Yours faithfully,

CHARLES BROOKE.

II. *A Remark on Differential Equations.*

By PROFESSOR CAYLEY, F.R.S.\*

CONSIDER a differential equation  $f(x, y, p) = 0$ , of the first order, but of the degree  $n$ , where  $f$  is a rational and integral function of  $(x, y, p)$  not rationally decomposable into factors: the integral equation contains an arbitrary constant  $c$ , and represents therefore a system of curves, for any one of which curves the differential equation is satisfied: the differential equation is assumed to be such that the curves are algebraical curves. The curves in question may be considered as indecomposable curves; in fact, if the curve  $U^\alpha V^\beta W^\gamma \dots = 0$  (composed of the undecomposable curves  $U=0, V=0, W=0, \dots$ ) satisfies the differential equation, then either the curves  $U=0, V=0, W=0, \dots$  each satisfy the differential equation, and instead of the curve  $U^\alpha V^\beta W^\gamma \dots = 0$  we have thus the undecomposable curves  $U=0, V=0, W=0$ , each satisfying the differential equation; or if any of these curves, for instance  $W=0$ , &c., do not satisfy the differential equation, then  $W^\gamma$ , &c. are mere extraneous factors which may and ought to be rejected, and instead of the original curve  $U^\alpha V^\beta W^\gamma \dots = 0$ , we have the undecomposable curves  $U=0, V=0$  satisfying the differential equation. Assuming, as above, the existence of an algebraical solution, this may always be expressed in the form  $\phi(x, y, c) = 0$ , where  $\phi$  is a rational and integral function of  $(x, y, c)$ , of the degree  $n$  as regards the arbitrary constant  $c$ : this appears by the consideration that for given values  $(x_0, y_0)$  of  $(x, y)$  the differential equation and the integral equation must each of them give the same number of values of  $p$ . It is to be observed that  $\phi$  regarded as a function of  $(x, y, c)$  cannot be rationally decomposable into factors; for if the equation were  $\phi = \Phi\Psi \dots = 0$ ,  $\Phi, \Psi$ , &c. being each of them rational and integral functions of  $(x, y, c)$ , then the differential equation would be satisfied by at least one of the equations  $\Phi=0, \Psi=0, \dots$  that is, by an equation of a degree less than  $n$  in the arbitrary constant  $c$ .

But the equation  $\phi(x, y, c) = 0$  is not of necessity the equation of an undecomposable curve, and the undecomposable curve which constitutes the proper solution of the differential equation cannot always be represented by an equation of the form in question. For although  $\phi$  regarded as a function of  $(x, y, c)$  is not rationally decomposable into factors, yet it may very well happen that  $\phi$  regarded as a function of  $(x, y)$  is rationally decomposable into factors (geometrically the sections by the planes  $z=c$  of the undecomposable surface  $\phi(x, y, z) = 0$  may each of them be com-

\* Communicated by the Author.



posed of two or more distinct curves); and assuming that the function  $\phi$  is thus decomposed into its prime factors, then each factor equated to 0 gives an undecomposable curve satisfying the differential equation, and constituting the proper solution thereof.

It may be observed that, by the foregoing process of decomposition, we sometimes reduce the original equation  $\phi(x, y, c) = 0$  into a like equation  $\phi_1(x, y, c_1) = 0$  of a more simple form. Thus, for instance, if we have  $\phi(x, y, c) = U^2 - c = 0$ ,  $U$  being a rational and integral function of  $(x, y)$ , then instead of  $\phi = U^2 - c = 0$  we have the equations  $U + \sqrt{c} = 0$ ,  $U - \sqrt{c} = 0$ , each of which is an equation of the form  $U - c_1 = 0$ , or we pass from the original equation  $\phi(x, y, c) = U^2 - c = 0$  to the simplified equation

$$\phi_1(x, y, c_1) = U - c_1 = 0.$$

Or, to take a somewhat more complicated instance, if the given integral equation be

$$\begin{aligned} \phi(x, y, c) = & U^4 + c^2 V^4 + (c+1)^2 W^4 \\ & - 2cU^2 V^2 - 2(c+1)U^2 W^2 - 2c(c+1)V^2 W^2 = 0, \end{aligned}$$

then the equation  $U + V\sqrt{c} + W\sqrt{c+1} = 0$ , writing therein

$$\sqrt{c} = \frac{2c_1}{c_1^2 - 1}, \text{ and therefore } \sqrt{c+1} = \frac{c_1^2 + 1}{c_1^2 - 1}, \text{ becomes}$$

$$U(c_1^2 - 1) + V \cdot 2c_1 + W(c_1^2 + 1) = 0;$$

so that we pass from the original equation  $\phi(x, y, c) = 0$  to the simplified equation

$$\phi(x, y, c_1) = U(c_1^2 - 1) + V \cdot 2c_1 + W(c_1^2 + 1) = 0.$$

But observe that the possibility of the rationalization depends on the form of the radicals  $\sqrt{c}$  and  $\sqrt{c+1}$ ; if we had had  $\sqrt{c}$  and  $\sqrt{c^2+1}$  (or  $c$  and  $\sqrt{c^4+1}$ ), the rationalization could not have been effected.

Returning to the case of an integral equation  $\phi(x, y, c) = 0$ , where  $\phi$  regarded as a function of  $(x, y)$  is decomposable into factors, then equating to zero any one of the prime factors of  $\phi$ , we obtain an integral equation  $\psi(x, y, c_1, c_2 \dots c_k) = 0$ , where  $c_1, c_2 \dots c_k$  are irrational functions (not of necessity representable by radicals, and without any superior limit to the number of these functions) of  $c$ : here  $\psi$  regarded as a function of  $(x, y)$  is of course undecomposable, and the equation  $\psi(x, y, c_1, c_2 \dots c_k) = 0$  belongs to the undecomposable curve which is the proper solution of the differential equation. The result may be stated under a quasi-geometrical form; viz. regarding  $c_1, c_2 \dots c_k$  as the coordinates of a point in  $k$ -dimensional space, then as these are functions of the single parameter  $c$ , the point to which they belong is an arbitrary point on a certain curve or  $(k-1)$ -fold locus  $C$  in



the  $k$ -dimensional space. And this curve must be such that to given values of  $(x, y)$  there shall correspond  $n$  points on the curve; that is, treating  $(x, y)$  as constants, the surface or one-fold locus  $\psi(x, y, c_1, c_2 \dots c_k) = 0$ , and the curve or  $(k-1)$ -fold locus  $C$ , shall meet in  $n$  points. The conclusion stated in the foregoing quasi-geometrical form is, that the solution of the differential equation may be exhibited in the form  $\psi(x, y, c_1, c_2 \dots c_k) = 0$ ; viz.  $\psi$  is a rational and integral function of  $(x, y, c_1, c_2 \dots c_k)$ , where  $(c_1, c_2 \dots c_k)$  are the coordinates of an arbitrary or variable point on a curve or  $(k-1)$ -fold locus  $C$  in a  $k$ -dimensional space, which curve meets the surface or one-fold locus  $\psi(x, y, c_1, c_2 \dots c_k)$  in  $n$  points, and where  $\psi$  regarded as a function of  $(x, y)$  is not rationally decomposable into factors.

Cambridge, October 13, 1866.

### LII. Chemical Notices from Foreign Journals.

By E. ATKINSON, Ph.D., F.C.S.

[Continued from vol. xxxi. p. 459.]

**B**ÖTTGER\* describes the following method of separating indium from the incrustation obtained from furnaces for roasting zinc. About 2 cwt. of incrustation was obtained from the chimney of the furnaces at the Juliushütte at Goslar. This deposit, in quantities of 6 to 8 pounds, was treated in spacious porcelain dishes with crude hydrochloric acid and boiled for half an hour. The liquid was then twice filtered through linen, and allowed to stand for six hours at the ordinary temperature in contact with thick sheets of zinc. The black velvety metallic powder which deposited was collected on a double filter, and washed with boiling water until the filtrate gave no longer any reaction for iron. The residue, consisting of copper, arsenic, cadmium, thallium, and indium, was boiled with hot concentrated solution of *oxalic acid*, the liquor diluted with much water, and filtered. The filtrate, which consisted of oxalate of indium containing cadmium and thallium, was precipitated with an excess of ammonia. The mucilaginous precipitate, resembling hydrate of alumina, still contained cadmium and thallium: it was boiled out a few times with ammonia, and then washed out with hot water until no more thallium could be detected by means of the spectroscope. If this hydrated oxide of indium still contained traces of iron, the latter metal was best separated by Winkler's method†. The oxide of indium was dissolved in hydrochloric acid, the iron reduced with sulphite of soda, and the cooled solution agitated for a few minutes with freshly precipitated carbonate of baryta, while car-

\* *Pol. Notizen*, vol. xxi. p. 177.

† *Phil. Mag. S. 4.* vol. xxx. p. 443.

bonic acid was simultaneously passed through the solution. It was dissolved in sulphuric acid, and then precipitated by ammonia. The amount of oxide of indium obtained was about 0.1 per cent.

Marignac gives an abstract\* of recent researches on the compounds of tantalum. Former researches had led him to attribute to niobic acid the formula  $Nb^2O^5$ †, and had taught him that this acid and tantalic acid were constantly associated in the mineral kingdom, and that they replaced each other without change of crystalline forms; he accordingly undertook the investigation of the principal compounds of tantalum, to establish for this metal the existence of a modification analogous to that proposed for niobium.

The first object was to redetermine the atomic weight of the metal. Analyses of chloride of tantalum executed by H. Rose led to the number 172 ( $H=1$ ,  $O=16$ ) for this atomic weight; but probably these analyses, made on a product doubtless containing chloride of niobium (for the presence of niobic acid in tantalates was at that time unknown), had given too small a number. The numerous analyses which he had made of the fluotantalates of potash and ammonia led him in fact to raise the number to 182.

These new determinations of the atomic weights of niobium and of tantalum, compared with those of the two metals which have the greatest analogy to each other (that is, tungsten and molybdenum), furnish a new and remarkable example of the parallelism which M. Dumas has noted between various series of simple substances forming natural groups. We have in fact, from his determinations,

Molybdenum . . . 96	Tungsten . . . 184;
and from Marignac's,	
Niobium . . . 94	Tantalum . . . 182.

The new composition admitted for tantalic acid leads to very simple formulæ for two bodies which appeared previously to have very complex compositions. The brown oxide of tantalum, which Berzelius obtained by calcining tantalic acid in a crucible lined with carbon, is a binoxide,  $TaO^2$ . In like manner sulphide of tantalum has, from the concordant analyses of Berzelius, Rose, and Hermann, the composition corresponding to the bisulphide,  $TaS^2$ .

Tantalic acid appears capable of forming two distinct modifications, analogous to those which Frémy's beautiful researches on stannic and antimonie acids have made us acquainted with. In fact the best-defined salts of this acid belong to two series

\* *Comptes Rendus*, July 16, 1866.

† *Phil. Mag.* S. 4. vol. xxx. p. 445.

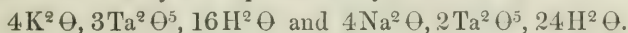
which have in their composition no simple ratios, and are not easily transformed into one another except by fusion with alkalies.

The first series corresponds to the general formula



It comprehends the natural Tantalite, and the insoluble compounds obtained by calcining tantallic acid with alkaline carbonates when the latter are in insufficient quantity, or when the calcination has not been strong enough or prolonged enough to give a completely soluble product.

The second series comprises the perfectly crystallized tantalates of potash obtained by melting tantallic acid with these caustic-alkalies, or with their carbonates, in excess at a very high temperature. They are represented by the formulæ



The first gives beautiful crystals, isomorphous with those of the corresponding niobate of potash.

These two salts had been obtained by H. Rose; and the results which he had obtained by analysis agree better with the formulæ which Marignac attributes to them than with those which he fancied himself obliged to adopt.

Fluoride of tantalum forms, with basic fluorides, fluosalts nearly all of which have the ratio 5 : 2 between the proportions of the fluorine of the two elements. The constancy of this ratio leaves no doubt as to the necessity of attributing to this fluoride the formula  $\text{Ta F}^5$ .

Except the fluotantalates of potash, of soda, and of ammonia, the other salts of this kind which were prepared are so soluble and even deliquescent that their crystalline form could not be determined.

The general analogy which exists between the compounds of niobium and those of tantalum ceases to be exhibited by their fluorides; for there do not appear to be any oxyfluotantalates. The correlation between these two groups of fluorized compounds is only established on a single point, by the existence of a fluoniobate of potash isomorphous with the fluotantalate.

The principal characteristic by which ordinary phosphorus is distinguished from red phosphorus is its property of crystallizing; yet it is by no means easily crystallized, although it possesses the triple property of being fusible, soluble, and volatile. Blondlot, having tried all the ordinary methods, had recourse to that of sublimation\*, which he describes as follows.

The neck of a flask was drawn out, at about an inch from the shoulder, to the thickness of a quill pen; and phosphorus

\* *Comptes Rendus*, August 27, 1866.



was melted under water in tubes of this dimension, and two grammes introduced in small fragments which were previously dried. That being done, the flask being held in a wet cloth, the neck was rapidly drawn out and sealed; this could be done without the phosphorus taking fire provided the flask was held vertically. The phosphorus was at first surrounded by whitish vapours, and shone in darkness; the interior then became clear, and the phosphorescence disappeared. In twenty-four hours all the oxygen was absorbed, and the phosphorus could then be melted, which was done in a water-bath heated by means of a small lamp. The flask was kept always in the same position, floating on water, the neck uppermost, by its being placed in a hole in the centre of a cork. Finally, to avoid the action of light, the whole was surrounded by a cone of cardboard.

After the lapse of a few hours, in the upper part of the flask, and even into the neck, small brilliant points are observed, which slowly increase and in two or three days are changed into a magnificent crystalline arborization which covers all the surface, and shines with all kinds of reflection and a lustre like that of the diamond. The crystals evidently belong to the cubical system. Many small crystals appeared to be regular cubes, and octahedra could also be observed. Independently of crystals applied against the sides, sometimes long salient needles having the aspect of fern leaves were observed.

In these experiments, if the phosphorus is suitably preserved from light it is of a beautiful white; but the moment it is struck, not merely by the solar rays, but even by diffused light, it passes in a few minutes into a garnet-red. In this new condition it retains its crystalline form, transparence, and its lustre; the crystals might be said to be small rubies. The crystalline form is then so little altered that, if the apparatus is replaced in the water-bath, new and perfectly white crystals are deposited on the red crystals. Hence red phosphorus does not deserve the term of amorphous which it generally receives—in this sense, that the character does not essentially belong to it, but arises from the difficulty, *à posteriori*, of crystallizing any body which, like it, is infusible, insoluble, and absolutely fixed.

Some of the thallic alcohols described by Lamy in 1864 are liquids characterized by their great refractive and dispersive powers; ethyl-thallic alcohol in particular is the most refracting of all known liquids. Lamy considered it probable that oxide of thallium, substituted for potash or minium in the composition of glass, would impart to it high refringent properties; and he accordingly undertook some experiments\* on the subject, at first

\* *Bulletin de la Société Chimique*, March 1866.



on a small scale, but subsequently at the manufactory of St. Gobain.

The various specimens prepared were obtained by taking ordinary flint-glass as the type, and successively replacing minium or carbonate of potash by carbonate of thallium in equivalent quantities. One specimen was made from sand, 300, pure carbonate of thallium, 400, and carbonate of potash, 100.

The glass resulting from this mixture readily fuses and refines, but the cooled mass is not homogeneous. The layers which occupy the upper part of the crucible have a less-pronounced yellowish colour, and a lower density, than the inferior layers, which are moreover richer in thallium.

Another specimen was obtained with the proportions:—sand, 300; minium, 200; pure carbonate of thallium, 335.

This mixture melts and is refined more easily than the preceding; the mass is perfectly homogeneous, but presents a yellowish tint, which, however, is agreeable and very brilliant. The density 4.235, and refractive index 1.71 (for the yellow ray), are greater than the corresponding elements of all known glasses. By varying the proportions in the mixture, Lamy obtained glasses whose densities varied from 4.235 to 5.625, and refractive indices from 1.71 to 1.965.

Lamy concludes, from the results of his experiments, (1) that thallium replaces potassium better than lead in the composition of glass, which is a new proof of the rank assigned to the new metal in the classification; (2) that thallium gives to glass a yellowish, as sodium does a greenish colour; (3) that thallium-glass is denser and more refringent than potassium-glass; (4) that these properties of thallium-glass may doubtless be advantageously used in making certain optical glasses or artificial precious stones.

There are in nature a number of minerals whose colour is sometimes very intense, and which become completely decolorized when they are heated to a certain temperature. The cause of this phenomenon is unknown; it is especially marked in the case of the fluorides, which Wyroutboff\* has investigated; from the results of his investigations he concludes

1. That the fluorides are of aqueous origin.
2. That the colouring-substances are various carburets of hydrogen, probably arising from bituminous limes, which by their decomposition have furnished the materials which have concurred in the formation of the fluoride.
3. That the odour of the fluorine of Wülsendorf† is due to the presence of a carburetted hydrogen accumulated in the fissures of the rock.

\* *Bulletin de la Société Chimique*, May 1866.

† *Phil. Mag.* S. 4. vol. xx. p. 515.

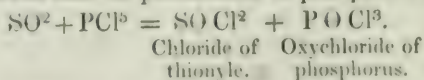
4. That the phosphorescence is only the result of the decomposition of the colouring-matter, and does not belong to fluor-spar itself.

It is commonly assumed that only distilled water attacks lead, but that saline water is without action. According to Stahlmann\*, if such a water contains 0.00001 to 0.0018 per cent. of  $\text{NH}^4\text{O}$ , it attacks the lead, becomes active. With a percentage of 0.0031  $\text{NH}^4\text{O}$  and above, the water is again indifferent, and no longer attacks the lead. If active water is boiled for an hour and a half, the attack on the metal is considerably weaker. If it is boiled with *carbonate of baryta*, it is all but indifferent. An addition of 0.006 per cent. of *nitric acid*, and less, makes the water active, any excess beyond that indifferent. Active water, neutralized with small quantities of ammonia and nitric acid, regained its former properties.

The attack of active water on lead is connected with the access of atmospheric air. Also in the presence of free carbonic acid access of air is a hindrance to corrosion; on the other hand, the contact of water with air appears to be insufficient if the air is free from carbonic acid. If a lead plate be placed in active water, the corrosion of the plate starts preferably from the place where the lead touches the bottom of the flask. When the lead was suspended in active water, it remained unattacked for a week. The precipitate was a hydrated carbonate of lead, the composition of which varied.

In the preparation of oxygen gas by the method of Fleitmann, by the action of peroxide of cobalt upon bleaching-powder†, a clear filtered solution is necessary; for a turbid one, or a mixture of chlorinated lime and water, froths up greatly and runs over. According to Stolbe‡, the tedious preparation of a clear solution may, however, be avoided by adding to a thick magma of the powder a few small pieces of paraffine. This melts on being heated, and covers the paste with a layer which prevents any frothing or rushing over. Instead of the peroxide of cobalt, the author states that a small quantity of a solution of nitrate or chloride of copper may be used, which, according to Böttger, acts just like the salts of cobalt. The disengagement of gas under these circumstances takes place very steadily and regularly.

Chloride of thionyle was obtained by M. Schiff by the action of dry sulphurous acid on perchloride of phosphorus,

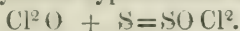


\* *Repertoire der Chemie*, July 1866.

† *Phil. Mag.* vol. xxx. p. 252.

‡ *Journal für praktische Chemie*, July 1866.

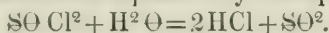
Wurtz has succeeded in obtaining chloride of thionyle by the direct action of anhydrous hypochlorous acid on sulphur,



Hypochlorous  
acid.

Gaseous hypochlorous acid was passed into subchloride of sulphur holding sulphur in solution, and the operation interrupted when the whole of the latter had disappeared. The chloride of thionyle, which boils at  $78^\circ$ , could be separated by fractional distillation from the subchloride of sulphur, which boils at  $139^\circ \text{C}$ .

It is a colourless liquid, of an irritating odour; its density at  $0^\circ$  is 1.675. Thrown into water, it at first falls to the bottom, and is then rapidly decomposed, just as is terchloride of phosphorus. The reaction is expressed by the equation



If, instead of diffusing the sulphur in an inert liquid like the subchloride, which must be cooled to  $10^\circ$  during the operation, the sulphur be projected into liquefied anhydrous hypochlorous acid, an explosion ensues.

In what are called abnormal vapour-densities it is assumed that a decomposition of the bodies takes place; and Deville has endeavoured to effect this decomposition in a visible manner\*. If pentachloride of phosphorus is heated in a closed tube in the oil-bath, and is thereby decomposed into  $\text{PCl}^3$  and  $\text{Cl}^2$ , the green colour of the gas must become visible. In order to show this, Deville filled two perfectly equal glass tubes, one with a mixture of equal volumes of chlorine and air, and the other with some pentachloride of phosphorus. Both were heated in the oil-bath; the tubes only projected to a small extent from the bath, so that a layer of gas 3 to 4 decimetres in thickness could be perceived. From a certain range of temperature onwards, the tube with the  $\text{PCl}^5$  is seen to be continually greener until it exhibits the same colour as the tube containing air and chlorine; but as long as the perchloride remains colourless, no decomposition takes place. Only then does dissociation occur; and from the known vapour-densities the tension of dissociation can be calculated.

A similar deportment is exhibited by the vapour of *iodide of mercury*. If this body be heated in a flask or retort above its melting-point, at a certain stage violet vapours are observed on the sides of the flask, which disappear in the interior of the vessel—that is, in the colder part. Here occurs, therefore, a recombination of the separated iodide. As a volume of iodine vapour and air equal in volume to this vapour exhibits a far more intense colour, the author assumes that at this temperature iodide-

\* *Comptes Rendus*, vol. lxii. p. 1157.



of-mercury vapour is not decomposed but only *dissociated*. The phenomenon is at the same time an instructive lecture experiment.

The above observations of Deville led Cahours\* to undertake new determinations of the vapour-density of  $\text{PCl}_5$ . This body boils between  $160^\circ$  and  $165^\circ$ ; and the density observed at  $170^\circ$  to  $172^\circ$ , though considerably greater than that at  $182^\circ$  to  $185^\circ$ †, was considerably below that calculated for a condensation to 4 volumes. The author could not observe a decomposition of pentachloride vapour at this temperature. Hence he assumes that the normal vapour of  $\text{PCl}_5$  occupies 8 volumes, corresponding to a union of  $\text{PCl}_3$  and  $\text{Cl}_2$  without condensation.

The vapour-density of *acetic acid*, determined at  $350^\circ$ , corresponded exactly to 4 volumes; but at  $440^\circ$  a considerably smaller number was obtained. It was found, however, that at this temperature a small quantity of marsh-gas and carbonic acid had been formed. Hence the author assumes that only condensations to 4 or 8 volumes occur. In the cases of apparent condensation to 3 or 6 volumes, it is only necessary to make the determination at a higher or lower temperature to obtain at once an alteration in the numbers.

Devilé‡ adduces a surprising instance of an abnormal vapour-density. The double salt  $\text{NH}_4\text{I}$ ,  $2\text{HgI}$  has, according to his and Troost's experiments, at  $350^\circ$  the vapour-density 6.49, and at  $440^\circ$  6.88, corresponding to a condensation to 8 volumes. Assuming in the experiment a dissociation into  $\text{NH}_4\text{I}$  and  $\text{HgI}$ , a condensation to 12 volumes should result.

Chizinski has made, under the direction of Dr. Lothar Meyer, an investigation on the influence of masses in chemical affinity§. He took solutions of chloride of calcium and of double chloride of magnesium and ammonium, and, having added to them relatively smaller quantities of ordinary tribasic phosphate of soda, determined the amounts of lime and magnesia precipitated on the addition of ammonia.

He found that the composition of the precipitate which contains lime and magnesia is not materially influenced by the presence of large quantities of water (that is, by the degree of concentration), nor by the quantity of ammonia added. Its composition depended essentially on the quantities of chloride of calcium and chloride of magnesium which were present. If in a series of experiments with one and the same quantity of phosphoric acid always the same quantity of chloride of magnesium, but variable

\* *Comptes Rendus*, vol. lxiii. p. 16.

† Liebig's *Jahresbericht*, 1847-48, p. 363.

‡ *Comptes Rendus*, vol. lxiii. p. 16.

§ Liebig's *Annalen* (Supplement), vol. iv. part 2. *Zeitschrift für Chemie*, April 1866.



quantities of chloride of calcium be added, with an increasing percentage of lime in the solution the proportion of lime in the precipitates also increases. And conversely, when the lime and the phosphoric acids are kept constant and the magnesia is increased, the percentage of magnesia in the precipitate increases.

As regards changes in the composition of the precipitate, Chizinski arrived at results differing from those which Debus obtained from his experiments on the affinity of carbonic acid for lime and baryta. Debus concluded that these changes took place by starts; Chizinski that they took place gradually and steadily. The quantity of any of the bases present in the precipitates increases if this is increased in the solution, but not, as Berthollet taught, proportionally to this increase. The composition of the precipitate varies in a rather complex manner with the composition of the solution.

If in the solution there are equivalent quantities of calcium and magnesium, more lime than magnesia is precipitated. Hence it may be assumed that, *ceteris paribus*, lime has a greater affinity for phosphoric acid than magnesia. But with equivalent quantities of both bases in solution, according as the mass of both as compared with the phosphoric acid is greater or smaller, the composition of the precipitate varies. If the solution for one molecule of phosphoric acid ( $\text{H}^3\text{PO}^4 = 98$ ) only contains one molecule of each base (that is,  $\text{CaCl}^2 = 110.92$  and  $\text{MgCl}^2 = 94.92$ ), the lime in the precipitate only slightly exceeds the magnesia; the sum of both is not quite equal to 3 equivalents (1 equivalent = half an atom of biatomic elements). Hence the precipitate must contain some ammoniacal phosphate of magnesium. If the quantity of bases in the solution is increased, the magnesia in the precipitate first decreases and then increases; the lime, however, continually and materially increases until, using  $10\text{CaCl}^2$  and  $10\text{MgCl}^2$  for  $1\text{H}^3\text{PO}^4$ , the precipitates contain 3 equivalents of lime and 1.1 equivalent of magnesia—that is, together more than 4 equivalents of base. These precipitates are basic phosphates, analogous to Wagnerite and Apatite, excepting that they contain no chlorine or fluorine, but oxygen instead.

If in the solution there is always one molecule of  $\text{MgCl}^2$  for one molecule of  $\text{H}^3\text{PO}^4$ , and the quantity of calcium salt in the various precipitates increases from one to ten molecules, not only does the proportion of lime in the precipitates increase while the magnesia decreases, but the sum of both bases increases from less than 3 to more than 4 equivalents for one molecule of phosphoric acid.

If, on the other hand, the proportion of lime in the solutions is constant (1.5 molecule = 3 equivalents), and if the quantity of magnesia is increased from one molecule for one molecule  $\text{H}^3\text{PO}^4$ ,

not only does the proportion of lime in the precipitate decrease while that of the magnesia increases, but the sum of the bases falls from 3 to a little less than 2 equivalents. With ten molecules,  $\text{Mg Cl}^2$ , in the solution, the precipitate is almost pure ammoniacal phosphate of magnesia with very little lime.

By comparing the experiments mentioned with those of Debus, the author finds that the latter will give results quite similar to his own, and that some of the conclusions which he deduces are to be regarded as not proved.

### LIII. *Proceedings of Learned Societies.*

#### ROYAL SOCIETY.

[Continued from p. 313.]

May 31, 1866.—Dr. W. A. Miller, Treas. & V.P., in the Chair.

THE following communication was read :—

“On the Dynamical Theory of Gases.” By J. Clerk Maxwell, F.R.S.L. & E.

Gases in this theory are supposed to consist of molecules in motion, acting on one another with forces which are insensible, except at distances which are small in comparison with the average distance of the molecules. The path of each molecule is therefore sensibly rectilinear, except when two molecules come within a certain distance of each other, in which case the direction of motion is rapidly changed, and the path becomes again sensibly rectilinear as soon as the molecules have separated beyond the distance of mutual action.

Each molecule is supposed to be a small body consisting in general of parts capable of being set into various kinds of motion relative to each other, such as rotation, oscillation, or vibration, the amount of energy existing in this form bearing a certain relation to that which exists in the form of the agitation of the molecules among each other.

The mass of a molecule is different in different gases, but in the same gas all the molecules are equal.

The pressure of the gas is on this theory due to the impact of the molecules on the sides of the vessel, and the temperature of the gas depends on the velocity of the molecules.

The theory as thus stated is that which has been conceived, with various degrees of clearness, by D. Bernoulli, Le Sage and Prevost, Herapath, Joule, and Krönig, and which owes its principal developments to Professor Clausius. The action of the molecules on each other has been generally assimilated to that of hard elastic bodies; and I have given some application of this form of the theory to the phenomena of viscosity, diffusion, and conduction of heat in the *Philosophical Magazine* for 1860. M. Clausius has since pointed out several errors in the part relating to conduction of heat; and the part relating to diffusion also contains errors. The dynamical theory

of viscosity in this form has been reinvestigated by M. O. E. Meyer, whose experimental researches on the viscosity of fluids have been very extensive.

In the present paper the action between the molecules is supposed to be that of bodies repelling each other at a distance, rather than of hard elastic bodies acting by impact; and the law of force is deduced, from experiments on the viscosity of gases, to be that of the inverse fifth power of the distance, any other law of force being at variance with the observed fact that the viscosity is proportional to the absolute temperature. In the mathematical application of the theory, it appears that the assumption of this law of force leads to a great simplification of the results, so that the whole subject can be treated in a more general way than has hitherto been done.

I have therefore begun by considering, first, the mutual action of two molecules,—next that of two systems of molecules, the motion of all the molecules in each system being originally the same. In this way I have determined the rate of variation of the mean values of the following functions of the velocity of molecules of the first system:—

$\alpha$ , the resolved part of the velocity in a given direction.

$\beta$ , the square of this resolved velocity.

$\gamma$ , the resolved velocity multiplied by the square of the whole velocity. It is afterwards shown that the velocity of translation of the gas depends on  $\alpha$ , the pressure on  $\beta$ , and the conduction of heat on  $\gamma$ .

The final distribution of velocities among the molecules is then considered; and it is shown that they are distributed according to the same law as the errors are distributed among the observations in the theory of “Least Squares,” and that, if several systems of molecules act on one another, the average *vis viva* of each molecule is the same, whatever be the mass of the molecule. The demonstration is of a more strict kind than that which I formerly gave; and this is the more necessary, as the “Law of Equivalent Volumes,” so important in the chemistry of gases, is deduced from it.

The rate of variation of the quantities  $\alpha$ ,  $\beta$ ,  $\gamma$  in an element of the gas is then considered, and the following conclusions are arrived at.

( $\alpha$ ) 1st. In a mixture of gases left to itself for a sufficient time under the action of gravity, the density of each gas at any point will be the same as if the other gases had not been present.

2nd. When this condition is not fulfilled, the gases will pass through each other by diffusion. When the composition of the mixed gases varies slowly from one point to another, the velocity of each gas will be so small that the effects due to inertia may be neglected. In the quiet diffusion of two gases, the volume of either gas diffused through unit of area in unit of time is equal to the rate of diminution of pressure of that gas as we pass in the direction of the normal to the plane, multiplied by a certain coefficient, called the coefficient of interdiffusion of these two gases. This coefficient must be determined experimentally for each pair of gases. It varies directly as the square of the absolute temperature, and inversely as the total pressure of the mixture. Its value for carbonic acid and air, as deduced from experiments given by Mr. Graham in his paper



on the Mobility of Gases\*, is

$$D=0\cdot0235,$$

the inch, the grain, and the second being units. Since, however, air is itself a mixture, this result cannot be considered final, and we have no experiments from which the coefficient of interdiffusion of two pure gases can be found.

3rd. When two gases are separated by a thin plate containing a small hole, the rate at which the composition of the mixture varies in and near the hole will depend on the thickness of the plate and the size of the hole. As the thickness of the plate and the diameter of the hole are diminished, the rate of variation will increase, and the effect of the mutual action of the molecules of the gases in impeding each other's motion will diminish relatively to the moving force due to the variation of pressure. In the limit, when the dimensions of the hole are indefinitely small, the velocity of either gas will be the same as if the other gas were absent. Hence the volumes diffused under equal pressures will be inversely as the square roots of the specific gravities of the gases, as was first established by Graham†; and the quantity of a gas which passes through a thin plug into another gas will be nearly the same as that which passes into a vacuum in the same time.

(β) By considering the variation of the total energy of motion of the molecules, it is shown that,

1st. In a mixture of two gases the mean energy of translation will become the same for a molecule of either gas. From this follows the law of Equivalent Volumes, discovered by Gay-Lussac from chemical considerations—namely, that equal volumes of two gases at equal pressures and temperatures contain equal numbers of molecules.

2nd. The law of cooling by expansion is determined.

3rd. The specific heats at constant volume and at constant pressure are determined and compared. This is done merely to determine the value of a constant in the dynamical theory for the agreement between theory and experiment with respect to the values of the two specific heats; and their ratio is a consequence of the general theory of thermodynamics, and does not depend on the mechanical theory which we adopt.

4th. In quiet diffusion the heat produced by the interpenetration of the gases is exactly neutralized by the cooling of each gas as it passes from a dense to a rare state in its progress through the mixture.

5th. By considering the variation of the difference of pressures in different directions, the coefficient of viscosity or internal friction is determined, and the equations of motion of the gas are formed. These are of the same form as those obtained by Poisson by conceiving an elastic solid the strain on which is continually relaxed at a rate proportional to the strain itself.

As an illustration of this view of the theory, it is shown that any strain existing in air at rest would diminish according to the values of an exponential term the modulus of which is  $\frac{1}{1100,000,000}$  second,

\* Philosophical Transactions, 1863.

† "On the Law of the Diffusion of Gases," Transactions of the Royal Society of Edinburgh, vol. xii. (1831).



an excessively small time ; so that the equations are applicable even to the case of the most acute audible sounds, without any modification on account of the rapid change of motion.

This relaxation is due to the mutual deflection of the molecules from their paths. It is then shown that if the displacements are instantaneous, so that no time is allowed for the relaxation, the gas would have an elasticity of form, or "rigidity," whose coefficient is equal to the pressure.

It is also shown that if the molecules were mere points, not having any mutual action, there would be no such relaxation, and that the equations of motion would be those of an elastic solid, in which the coefficient of cubical and linear elasticity have the same ratio as that deduced by Poisson from the theory of molecules at rest acting by central forces on one another. This coincidence of the results of two theories so opposite in their assumptions is remarkable.

6th. The coefficient of viscosity of a mixture of two gases is then deduced from the viscosity of the pure gases ; and the coefficient of interdiffusion of the two gases. The latter quantity has not as yet been ascertained for any pair of pure gases ; but it is shown that sufficiently probable values may be assumed, which being inserted in the formula agree very well with some of the most remarkable of Mr. Graham's experiments on the Transpiration of Mixed Gases\*. The remarkable experimental result that the viscosity is independent of the pressure and proportional to the absolute temperature is a necessary consequence of the theory.

( $\gamma$ ) The rate of conduction of heat is next determined, and it is shown,

1st. That the final state of a quantity of gas in a vessel will be such that the temperature will increase according to a certain law from the bottom to the top. The atmosphere, as we know, is colder above. This state would be produced by winds alone, and is no doubt greatly increased by the effects of radiation. A perfectly calm and sunless atmosphere would be coldest below.

2nd. The conductivity of a gas for heat is then deduced from its viscosity, and found to be

$$\frac{5}{3} \frac{1}{\gamma - 1} \frac{p_0}{\rho_0 \theta_0} \frac{\mu}{S},$$

where  $\gamma$  is the ratio of the two specific heats,  $p_0$  the pressure, and  $\rho_0$  the density of the standard gas at absolute temperature  $\theta_0$ ,  $S$  the specific gravity of the gas in question, and  $\mu$  its viscosity. The conductivity is, like the viscosity, independent of the pressure, and proportional to the absolute temperature. Its value for air is about  $\frac{1}{35000}$  of that of wrought iron as determined by Principal Forbes. Specific gravity .0069.

For oxygen, nitrogen, and carbonic oxide, the theory gives the conductivity equal to that of air. Hydrogen according to the theory should have a conductivity seven times that of air, and carbonic acid about  $\frac{7}{5}$  of that of air.

\* Philosophical Transactions, 1846.

LIV. *Intelligence and Miscellaneous Articles.*

THEORETICAL AND EXPERIMENTAL RESEARCHES ON THERMO-ELECTRICAL CURRENTS. BY M. F. P. LE ROUX.

THE investigation I have to submit to the judgment of the Academy is divided into nine parts.

1. In the first I investigate the conditions of a celebrated experiment by Becquerel relative to the production of a thermoelectric current in a wire twisted in one place. I then show that the condition necessary for the production of the current is the contact of two parts of the wire whose temperatures are different—an opinion which indeed had been already expressed by M. Gaugain. The conclusion, then, to be drawn from the point of view of the possible cause of the disengagement of electricity by heat is, that this cause would not be in the inequality in quantity of the flux of heat transmitted on both sides the heated point.

2. The second paragraph is devoted to the discussion of the thermoelectric effects produced on the contact of two masses of the same nature and different temperatures. I point out a cause, not yet remarked, which evidently influences the disengagement of electricity observed in this case. It is based on the fact, shown successively by M. Babinet and by Mr. W. Thomson, and which I investigate in this memoir, that two fragments of the same metal, one in the natural condition and the other stretched, present thermoelectrical effects when the temperature of their point of contact is raised.

3. In the third paragraph I give the results of experiments which I have made on the thermoelectrical relations existing between two wires of different metals, one stretched and the other in the natural state. I examined eight metals, Mr. W. Thomson three. My results are in the opposite direction to his for two of the metals—iron and platinum.

4. In the fourth paragraph I analyze the various theories proposed to account for the effect of heat on the production of thermoelectrical currents; I call to remembrance the important discovery made by Mr. W. Thomson, of the fact that when electricity traverses a conductor going from a hot to a cold part, it can, according to the nature of the conductor, disengage or absorb heat, and *vice versa*.

5. The fifth paragraph commences by the establishment of a paragraph formulated, I believe, for the first time:—*When in a circuit absorptions or disengagements of heat are produced proportional to the simple power of the intensity of the current, these effects correspond proportionally to electromotive forces promoted or overcome.*

This proposition opens a new path for discovering the seat of electromotive forces and valuing their absolute intensity, while measurements of the intensity of currents only give us the algebraic sums of the various forces which may exist in a circuit. As regards thermoelectric currents, it must be concluded that the effects discovered by Peltier and by Mr. W. Thomson point out the existence of electromotive forces and enable them to be measured.

What is the part of each of these kinds of electromotive forces (which I shall speak of as *Peltierian* and *Thomsonian*)? This is examined in the next paragraph.

6. In this sixth paragraph I first estimate the calorific effects of a

certain current, taken as unity, in passing from copper to the metals afterwards designated. By comparing the number of thermal units found with the thermic equivalent of the chemical effects produced by a current of the same intensity in a sulphate-of-copper element (in which voltaic and chemical heat appear to be exactly equal), I can compare with the electromotive force of this element the electromotive forces of the Pelterian kind which exist at the junction of the copper with the metal after it. I thus find that at a temperature of 25° these electromotive forces are represented by the following fractions:—

Copper-antimony and cadmium alloy of M. Becquerel	$\frac{1}{67}$
Copper-antimony .....	$\frac{181}{181}$
Copper-iron .....	$\frac{349}{349}$
Copper-zinc .....	$\frac{271}{271}$
Copper-cadmium .....	$\frac{1}{1917}$
Copper-brass .....	$\frac{1}{345}$
Copper-bismuth .....	$\frac{1}{46}$
Copper-bismuth and antimony of M. E. Becquerel.	$\frac{1}{34}$

I then seek to know if, for the couple copper-bismuth of M. E. Becquerel, the variation of this force between two temperatures, 25° and 100°, can account for the electromotive force between the same limits of temperature, a force which M. Becquerel estimated by taking as unit a sulphate-of-copper couple. With this view I measure in an appropriate stove the Pelterian effects at the two temperatures indicated; I find between the result predicted and that given by experiment a slight difference. But it is not the less constant that in this couple the electromotive forces of the Pelterian kind are much predominant.

7. The seventh paragraph is devoted to the investigation and measurement of the Thomsonian effect.

I have commenced by verifying that the Thomsonian effect was proportional to the intensity of the current.

The effect in question may be altered by several disturbing causes—want of homogeneity, tempering, twisting, crystalline texture, &c. These are effects of the Pelterian kind; they are proportional to the intensity of the current, but they change the sign when, other things being equal, end for end the conductors are changed; hence this gives a method of eliminating disturbing causes by two operations made on the same conductors reversed.

8. In the eighth paragraph I attempt to value the relative part of the electromotive forces of the Pelterian and of the Thomsonian kind. From the point of view of the direction, it is found that in Becquerel's copper-bismuth couple and in the copper-iron couple (before inversion) these two kinds of electromotive force add on to one another.

9. From what precedes, leaving aside the Thomsonian effects, it may be regarded as an experimental law that thermoelectric couples are proportional for all couples, between the same temperatures, to the electromotive forces which have their seat at the surfaces of junction. In other words, the electromotive force is for each a function of the temperature; the ratio of a finite variation of the value of this function to the value of this function for determinate temperatures is the same for all couples, which requires that this function of the temperature be the same for all except for a very small factor.



But since, from a law very long ago propounded by M. Becquerel, each metal bears in all the couples the same thermoelectric relation, the electromotive force which has its seat at the junction of the two metals must have the form  $aF(t) + bF(t)$ . As, moreover, electromotive force and electrical tension are synonymous terms, we are led *à priori* to the conclusion that each body possesses an electrical tension measured by the product of a function of the temperature identical for all bodies, and of a coefficient special for each of them.

What is this function of the temperature? Other experiments will perhaps enable me to determine this. But the identity of this function leads us to conclude that thermo-electricity is a property of matter, and not an accident of a substance.

As to the conception of an absolute electrical tension, a function of the temperature, I think it is destined to account for many phenomena, especially atmospheric electricity, to solve the difficulty of the preexistence of chemical action or of electrical action, and to make, finally, a new step towards the identification of heat with electricity. —*Comptes Rendus*, August 20, 1866.

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ON A MEANS OF WEAKENING THE SOLAR RAYS IN THE FOCUS OF  
TELESCOPES. BY M. LEON FOUCAULT.

When the physical constitution of the sun is to be studied by means of the large instruments in observatories, it is necessary to have recourse to some methods for diminishing the intensity of the light and heat which are concentrated in the focal image.

By placing a dark glass before the eyepiece, the eye is protected for the first few minutes against the intensity of the radiation; but if the observation be prolonged, and the object-glass has a large eyepiece, the glass becomes heated and is finally broken, the observer being thus exposed to the direct action of the sun's rays.

Sometimes it has been attempted to remedy this inconvenience by reducing the field of the object-glass by a diaphragm; but this method only injures the optical effect, and therefore will not bear examination.

It has further been proposed to make the pencil undergo a partial reflexion under the angle of polarization, and to provide the eyepiece with an analyzer whose azimuth is varied so as to diminish at will the intensity of the rays which traverse it. By this means the images are weakened without any appreciable coloration being imparted to them; but it is seldom that they are subjected to this complicated treatment without appreciably diminishing the precision of the image: the instrument loses its optical power; and this is just what must be avoided if we are to obtain from the use of large telescopes all they can teach us respecting the revolutions which take place on the star.

Having been led by my researches on the telescope to silver a large number of glass mirrors, I have often had occasion to remark that the metallic layer whose lustre is so brilliant possesses at the same time a transparence and limpidity comparable to that of the most beautiful coloured glasses. The transparence is so great that, looking at the sun through the thin layer of silver, the least vapours passing over its surface are seen distinctly and without the least fatigue. I was naturally led to suppose that a silvered glass might



replace coloured glasses, and that it would have over these latter the great advantage of reflecting all rays which do not pass through it. Most certainly a glass plate silvered on one face and placed in the body of the telescope in the path of the beam, would present a convenient means of viewing the sun.

But as this layer of silver might be regarded as a medium without thickness, I thought it would be better to silver the object-glass itself, and to leave quite untouched the arrangement of the telescope.

I did not alter the eyepieces; I left the micrometer in its place, and confined myself to silvering the outside of the object-glass. By this means the instrument is protected against the ardour of the sun's rays, which are almost entirely reflected towards the heavens, while the small portion of bluish light which traverses the layer of metal is refracted in the ordinary manner, and forms in the focus a pure and calm image which may be observed without danger to the sight.

The contour of the disk stands out distinctly on a dark sky, the spots are well defined, the faculæ are distinctly seen as well as the decrease of light towards the edges, and the observer immediately feels that he is provided with a powerful means of investigation. The true tint of the sun is a little altered by the predominance of the blue rays; but the ratios of intensity are so well preserved that no detail is lost, and after a certain time the eye, accustomed to this bluish colour, ceases to be conscious of it.

It is true that a telescope thus prepared is an instrument sacrificed, at all events for a time, to a single object. Perhaps it will be found that the object is worth the sacrifice. At a time when the greatest questions are discussed regarding the physical constitution of the sun, when the newest and most ingenious lights tend to unveil the mechanism of such a prodigious effusion of heat and light, it will doubtless not be uninteresting to try an application on a large instrument.

In reply to a question put by M. Chevreul as to whether in the case of gold-leaf blue light is transmitted through the substance of the gold, or simply passes through the numerous interstices of a plate reduced by mechanical means to so slight a thickness, M. Foucault said that in his opinion the blue coloration of light transmitted through gold-leaf proves that this metal, like silver, can allow light to pass by a real transparency, but that this does not prevent the gold in this extreme degree of fineness from affording numerous chinks invisible to the microscope, and which allow a certain quantity of direct light to pass. Something of the same kind is met with in the case of silver deposited under certain conditions, although the microscope does not furnish a proof. When the reagents are put together the proportions may be altered, and the layer ceases to present its characteristic blue tint. Everything leads to the belief that the layer of metal thus formed has not a perfect continuity; for by rubbing the metallic surface with a skin its metallic lustre is increased, the quantity of transmitted light diminished, and the blue colour made to reappear. Evidently under the pressure of the burnisher the silver is extended, the pores are closed, and the light can now only pass through the silver itself. What is here proved for gold and for silver would doubtless apply to all metals if they could be reduced into sufficiently fine plates.—*Comptes Rendus*, Sept. 3, 1866.

ON THE PASSAGE OF THERMAL AND LUMINOUS RAYS THROUGH  
INCLINED DIATHERMANOUS AND TRANSPARENT PLATES. BY  
H. KNOBLAUCH.

On the occasion of an investigation instituted by the author in the year 1847 on the polarization of heat by simple refraction\*, he had observed that *solar rays traversed a number of parallel glass plates which originally were placed at right angles to them, the more copiously the more they were inclined*, which was the more surprising as with an increasing thickness of the layer a diminished intensity would rather have been expected.

This increase was still further increased if the thermal rays reaching the glass through a Nicol's prism were polarized in such a manner that *their plane of polarization was at right angles to the refractive index of the glass plates*. If, for instance, a Nicol placed in a window was horizontal, and hence the plane of polarization of the rays passing through vertical—if, further, the upright glass plates were moveable about a vertical axis, the horizontally refracted thermal rays, caught completely at each inclination of the glasses on a thermopile, produced the following deflections on a multiplier connected with it:—

Angle which the thermal rays formed with the normal to the glass plates.	Deflection on the thermomultiplier on the passage of the heat-rays through			
	3 plates.	6 plates.	9 plates.	12 plates.
0	16.00	10.50	7.00	4.50
20	17.25	11.50	8.00	4.50
40	17.25	13.00	10.25	8.75
60	19.50	13.75	12.00	10.50

Although these observations had not the object of ascertaining those transmissions, and were not made in a series to be comparable for the present case, they prove beyond doubt that, at all events within wide limits,—

I. *The capacity of thermal rays* of traversing parallel glass plates increases with the angle which they form with the normal to the glass plates.

II. This capacity increases with the number of plates.

If, owing to a rotation of a Nicol's prism through 90°, *the plane of polarization of the rays entering coincided with the refractive index of the piece of glass*, the heat which passed through produced the following actions on the thermoscope:—

Angle which the thermal rays formed with the normal to the glass plates.	Deflection on the thermomultiplier on the passage of the heat-rays through			
	3 plates.	6 plates.	9 plates.	12 plates.
0	16.00	10.50	7.00	4.50
20	16.00	10.50	6.37	2.37
40	12.75	8.00	5.00	2.37
60	10.25	4.00	1.00	0.00

\* Poggendorff's *Annalen*, vol. lxxiv. p. 170.

These numbers, which also require a special revision, prove that the passage of radiant heat under the present conditions is just the opposite of the foregoing:—

I. *Decreases the more the angle of inclination increases.*

II. *That this decrease is greater the greater the number of plates.*

In the year 1854 Professor Schweigger\* showed that an object seen through several plates appears brighter if an acute position is given to the plates, than if it is looked at through the smallest diameter. In this manner the fact found for heat was shown for light.

In making his experiment, Schweigger had been led by an observation mentioned by Schülen†, according to which the image of a telescope is made more distinct by placing the object-glass at an acute angle; this he proposed to strengthen by several glasses according to the principle of the electromagnetic multiplier, “to form from it a lecture experiment.” Any further explanation or proof of a connexion with other optical processes is not met with‡.

To ascertain, if possible, such a connexion, and also to establish the limits of the phenomenon as far as it overcomes the counteracting absorption of the irradiated substance, the author has since then again taken up the subject.

It has been established without any doubt *that the maximum intensity of thermal as well as luminous rays traversing colourless glass pieces is attained at the polarizing angle—that is, at an inclination of about  $55^\circ$  to the normal; and from that point a rapid and increasing diminution sets in.*

Thus with, twelve glasses, in the passage from  $50^\circ$  to  $55^\circ$  there was an increase of the thermal action (which for measurements is far more certain than the optical estimation) from 10·32 to 10·60—that is, 3 per cent.; from  $55^\circ$  to  $60^\circ$ , a diminution of 10·60 to 9·25—that is, 1·3 per cent.

With rays whose *plane of polarization is at right angles to the plane of refraction* of the glass piece, under the same angle of inclination, the deflection of the galvanometer-needle increased from  $9^\circ$  to  $9^\circ\cdot5$ —that is, 6 per cent.; with a continued inclination it decreased from  $9^\circ\cdot5$  to  $8^\circ\cdot75$ ,—that is, 8 per cent. Hence the increase in this case is greater, the decrease smaller than in the previous case.

When *the original plane of polarization and plane of refraction of the plates traversed coincided*, the diminution of intensity continued during the further inclination, although to a diminished extent. With the same twelve glasses it amounted, for the change of angle from  $50^\circ$  to  $55^\circ$  to 2·19 to 1·19—that is, 46 per cent.; for the change from  $55^\circ$  to  $60^\circ$ , from 1·19 to 0·76—that is, a change of 34 per cent.

On *coloured glasses* or other substances, such as mica, isinglass of various colours, bluish-green transparent gold lamellæ, along with the phenomenon mentioned, *absorption* was observed in a decided manner.

With plates of yellow glass or of mica it was manifest how the increase of intensity with increasing inclination, and the simulta-

\* “On the Optical Significance of the principle exhibited on the Electromagnetic Multiplier for strengthening the Magnetic Swing,” *Abhandlungen der naturforschenden Gesellschaft zu Halle*, vol. xi. p. 201.

† Contributions to the Dioptries and History of Glass. By Max. Ludwig Christoff Schülen, Pastor of Esslingen in Swabia. Nördlingen, 1782.

‡ A communication recently published by Prof. Magnus, which, according to a private communication, treats the same subject, has not reached the author.



neous absorption on account of the greater thickness, held one another in check, so that the action of the rays was not perceptibly changed until the angle of  $55^\circ$  was attained, upon which there was a sudden diminution of the transmission. With a uniformly darker colouring of the plates, the diminution in intensity might take place before that angle was attained; yet the diminution then was never so sudden and considerable.

A corresponding deportment was observed with other bodies. Gold, on account of its considerably larger angle of polarization, of about  $70^\circ$ , was very characteristic.

When there was no absorption, the thickness and number of plates had no influence on the angle of inclination at which the transmission attained its maximum, as this always occurred at the polarizing angle of the substance in question. Yet with absorbing layers it depends on their *thickness* and the *degree of their absorption*, whether, and at what number of plates an increase of transmission takes place at all, and whether diminution only occurs at the polarizing angle, or whether, when absorption preponderates, it occurs before.

If it be considered that, from the observations communicated, the rays are the more capable of entirely or partially traversing transparent or diathermanous plates, the more completely they are polarized in a plane at right angles to their plane of refraction, the greater the number of these plates, and the more their inclination towards the rays approaches the polarizing angle—and if it be assumed that refracting plates polarize heat, as well as light, more completely at right angles to the plane of refraction\* the greater their number and the more their inclination approaches the angle in question †, it will at once be seen how the row of plates put the rays which enter them more and more into the condition of penetrating the succeeding ones with greater facility, and how the conditions for making the rays in the given case more capable of transmission coincide with those under which the layers themselves opposed to these become more permeable.

As polarization by simple refraction is, in the most favourable case, most nearly complete by a Nicol's prism‡, it is always explicable why polarization through a Nicol effects a greater increase of intensity of the transmitted rays when its plane of polarization coincides with that of the refracting piece, than does the glass piece alone.

On the other hand, the difference between the increase on attaining, and the diminution on exceeding the angle of polarization, must be smaller in the former case than in this; for in the former case the polarization of the rays is throughout unchanged, and transmission is only favoured by the position of the plates; for instance, in the case of glass it is favoured between  $50^\circ$  and  $55^\circ$ , diminished from  $55^\circ$  to  $60^\circ$ ; in the plane piece of glass the polarization of the rays and the influence of the plates on the transmission are simultaneously changed; at first both are increased, afterwards both diminished; the passage through the polarizing angles is hence the more marked.

But among the elucidations which refer the present case to more general points of view, it loses its surprising character; the more copious transmission of the thermal or luminous rays incident in the natural condition through inclined diathermanous or transparent plates follows as a direct consequence.—Poggendorff's *Annalen*, May 1866.

\* Pogg. *Ann.* vol. cxxiv. p. 175. † Ibid. p. 176. ‡ Ibid. p. 178.



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LV. *On the Absorption and Dialytic Separation of Gases by Colloid Septa.* By THOMAS GRAHAM, F.R.S., Master of the Mint\*.

PART I.—*Action of a Septum of Caoutchouc.*

MIXED gases must differ considerably in diffusibility and specific gravity, in order to separate from one another to any great extent in their molecular passage into a vacuum through a porous septum, such as the plate of graphite or the walls of an unglazed earthenware tube. The agency of atmolysis is therefore very limited in parting the oxygen and nitrogen of atmospheric air—gases which differ so little in density from each other.

Substances existing in the liquid condition often admit of being separated much more fully than gases, by the proper use of dialytic septa in addition to the agency of liquid diffusion.

Evidently there cannot be anything like the dialysis of gases; for dialysis involves the passage of a substance through a septum composed of soft colloid matter, such as must be wholly destitute of open channels, and therefore be impermeable to gas as such. Still liquid dialysis may be imported into the treatment of gases, in consequence of the general assumption of liquidity by gases when absorbed by actual liquids or by soft colloids. Water when charged with air holds liquid oxygen and nitrogen in solution; and the latter substances then become amenable to liquid diffusion and dialysis, and so penetrate animal membrane in the act of respiration.

A considerable time ago Dr. Mitchell of Philadelphia disco-

\* From the Philosophical Transactions for 1866, part 2. Communicated by the Author.

vered a power in gases to penetrate india-rubber in a thin sheet, or in the form of the little transparent balloons which Dr. Mitchell was the first to prepare from that substance. He remarked in particular that such balloons collapse sooner when inflated with hydrogen than with atmospheric air, and still sooner when filled with carbonic acid; and he connected the latter fact with the observation that a solid piece of india-rubber is capable of absorbing its own volume of carbonic acid when left long enough in the pure gas. By means of a proper arrangement, Dr. Mitchell found that various gases passed spontaneously through the caoutchouc membrane *when there was air on the other side*, with different degrees of velocity. "Ammonia transmitted in 1 minute as much as sulphuretted hydrogen in  $2\frac{1}{2}$  minutes, cyanogen in  $3\frac{1}{4}$  minutes, carbonic acid in  $5\frac{1}{2}$  minutes, nitrous oxide in  $6\frac{1}{2}$  minutes, arseniетted hydrogen in  $27\frac{1}{2}$  minutes, olefiant gas in 28 minutes, hydrogen in  $37\frac{1}{2}$  minutes, oxygen in 1 hour and 53 minutes, carbonic oxide in 2 hours and 40 minutes." The rate of penetration of nitrogen appeared to be even slower than that of carbonic oxide\*.

It will be observed that those gases penetrate most readily which are easily liquefied by pressure, and which are also "generally highly soluble in water or other liquids." The memoir of Dr. Mitchell was ably commented upon, shortly after its publication, by Dr. Draper of New York, who also added many new observations on the passage of both gases and liquids through membranous septa†. These early speculations, however, lose much of their fitness from not taking into account the two considerations already alluded to, which appear to be essential to the full comprehension of the phenomena—namely, that gases undergo liquefaction when absorbed by liquids and such colloid substances as india-rubber, and that their transmission through liquid and colloid septa is then effected by the agency of liquid and not gaseous diffusion. Indeed the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view.

Dr. Mitchell was led to infer, from a single casual observation, that rubber expands in volume when carbonic acid is absorbed—a result to be expected from the porosity of the solid mass, then assumed in explanation of the penetrativeness of gaseous fluids. But on placing 50 grms. of thin sheet rubber, 0.6 millim. in

\* "On the Penetrativeness of Fluids," by J. K. Mitchell, M.D.—Philadelphia Journal of Medical Sciences, vol. xiii. p. 36; or Journal of the Royal Institution, vol. ii. pp. 101 & 307 (London, 1831).

† A Treatise on the forces which produce the organization of Plants, with an Appendix containing several Memoirs on Capillary Attraction, Electricity, and the Chemical Action of Light, by John William Draper, M.D.

thickness, in carbonic acid over mercury, it was seen that the rubber gradually absorbed 0.78 volume of gas in twenty-four hours at  $15^{\circ}$ , of which 0.7 volume was taken up in the first hour. The mass of rubber was previously measured with care by the displacement of mercury in a specific-gravity bottle, and again when the rubber was charged with carbonic acid; it gave the same displacement of mercury within a hundredth of a gramme. No measurable change in the bulk of the rubber, therefore, had occurred. It may be added that the absorbent power of vulcanized rubber for carbonic acid appears to be less than that of rubber in its natural state, being found only 0.57 volume in a comparative experiment.

The penetration of rubber by gases may be illustrated by their passage into a *vacuum*, as well as into an atmosphere of another gas in Dr. Mitchell's experiments. The diffusiometer, consisting of a plain glass tube of about 22 millims. in diameter and nearly a whole metre in length, closed at the upper end by a thin plate of stucco and open below, is taken advantage of in such experiments. A thin film of rubber from a small balloon is stretched over the upper end of the tube, where it is supported by the stucco plate, bound with copper wire, and cemented at the edges in contact with the glass with gutta percha softened by heat. If the tube be now filled with mercury and inverted, a Torricellian vacuum is obtained above, into which the air of the atmosphere gradually penetrates, passing through the film of rubber and depressing the mercurial column in the tube. In order to compare the penetration of different gases, a hood of thick vulcanized rubber, provided with a small entrance- and exit-tube for gas (such as is often used in gas experiments), is placed over the upper end of the diffusiometer described, and cemented to it by means of fused gutta percha. The gas to be operated upon can thus be conveyed from the apparatus in which it is generated, or from a gasometer in which the gas is stored, into the hood or upper chamber of the diffusiometer, and the excess of gas supplied be allowed to escape into the atmosphere by the exit-tube of the hood. The stucco plate used as a support to the film of rubber is so highly porous as not to add sensibly to the resistance experienced by the gases in passing through the rubber, and, having no absorbent power of its own, may be left entirely out of consideration.

A comparison was made of the passage through the rubber film, on the same day, of carbonic acid, hydrogen, oxygen, and nitrogen; barom. 773 millims., therm.  $23^{\circ}$  to  $23.5^{\circ}$  C. The time during which the mercurial column fell in the diffusiometer from 748 to 723 millims. was noted in seconds, and also from 723 to 698 millims. The gases were all carefully dried.

TABLE I.—Passage of Carbonic Acid, in seconds.

Height of mer- curial column in diffusio- meter.	Experiment 1.	Experiment 2.	Experiment 3.
millims.			
748			
723	107 <sup>''</sup>	102 <sup>''</sup>	102 <sup>''</sup>
698	143	138	138
	250	240	240

The passage of carbonic acid thus exhibited will be found to be considerably more rapid than those of hydrogen and the two other gases which follow :—

TABLE II.

Height of mer- curial column in diffusio- meter.	Passage, in seconds,					
	of Hydrogen.		of Oxygen.		of Nitrogen.	
	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.
millims.						
748						
723	277 <sup>''</sup>	270 <sup>''</sup>	545 <sup>''</sup>	554 <sup>''</sup>	1413 <sup>''</sup>	1428 <sup>''</sup>
698	316	323	727	722	1832	1850
	593	593	1272	1276	3245	3278

A single experiment, made at the same time, on the passage of atmospheric air, gave times of 1318<sup>''</sup> and 1524<sup>''</sup> for the two stages, or 2842<sup>''</sup> for the whole fall. The time of penetration of air is therefore intermediate between that of oxygen and nitrogen entering singly.

Although such numbers do not possess the close uniformity which appears in diffusion- and transpiration-experiments, for reasons which will immediately appear, yet they give a comparative estimate of the penetrativeness of the different gases through rubber, which may be available for some practical purposes.

Upon another occasion carbonic oxide and marsh-gas ( $\text{C H}_4$ ) were introduced into the comparison, the same film of rubber remaining upon the diffusimeter; barom. 768 millims., therm. 19°·5 C.



TABLE III.

Height of mercurial column in diffusio- meter.	Passage, in seconds,								
	of Carbonic oxide.		of Hydrogen.		of Carbonic acid.			of Marsh-gas (CH <sup>4</sup> ).	
	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.	Exp. 3.	Exp. 1.	Exp. 2.
millims.									
748	1620	1631	435	434	125	119	117	803	821
723	1920	1924	505	511	170	169	172	1009	1045
698									
	3540	3555	940	945	295	288	289	1812	1866

The results may be summed up by deducing the times in which a constant volume of the various gases is transmitted by the rubber,—the time of passage of carbonic acid, which is the shortest, being taken as unity for the sake of comparison.

Penetration of rubber by equal volumes of Gas.

	Time.
Carbonic acid . . . . .	1
Hydrogen . . . . .	2·470
Oxygen . . . . .	5·316
Marsh-gas (CH <sup>4</sup> ) . . . .	6·326
Atmospheric air . . . .	11·850
Carbonic oxide . . . . .	12·203
Nitrogen . . . . .	13·585

Or, with the times taken equal, the volume of each gas which passes then expresses the velocity of penetration.

Penetration of rubber in equal times.

	Velocity.
Nitrogen . . . . .	1
Carbonic oxide . . . . .	1·113
Atmospheric air . . . .	1·149
Marsh-gas (CH <sup>4</sup> ) . . . .	2·148
Oxygen . . . . .	2·556
Hydrogen . . . . .	5·500
Carbonic acid . . . . .	13·585

Considering the circumstances in which the gases pass through the sheet of rubber into a vacuum, it is not to be expected that any relation will be found among the preceding numbers, as between the coefficients of diffusion in gases. The first absorption

of the gas by rubber must depend upon a kind of chemical affinity subsisting between the material of the gas and substance of rubber, analogous to that attraction which is admitted to exist between a soluble body and its solvent, conducing to solution. Carbonic acid being soluble in ether and volatile oils, it is not wonderful that it is also dissolved by the hydrocarbons of rubber. The rubber being *wetted through* by the liquefied gas, the latter comes to evaporate into the vacuum, and reappears as gas on the other side of the membrane. Now it is known that such evaporation is the same into a vacuum and into another gas, being equally gas-diffusion in both circumstances. It is not indispensable, therefore, to have a vacuum on one side of the rubber membrane as in the experiments detailed above. A foreign gas will answer for the vacuum, as in the experiments of Dr. Mitchell.

The numbers for the velocity of passage of the different gases in the last Table may be taken also as representing not remotely the relative absorption and liquefaction of the various gases by the substance of rubber.

The passage of gases through rubber is also illustrated by the rapid collapse of the little balloon when filled with carbonic acid gas, or even with hydrogen, or with marsh-gas, as compared with atmospheric air. The converse fact is observed when the inflating gas is pure nitrogen: then the balloon is found to become further distended after a few hours, in consequence of more oxygen entering from the atmosphere without, than of nitrogen escaping from the balloon during the same time; while the composition is being equalized on both sides of the membrane, and the gas within the balloon is finally of the same composition as the external air. A rubber balloon filled with nitrogen was found, when roughly gauged, to increase in diameter from 132 to 136 millims. in the course of twenty-four hours. On the other hand, a balloon filled with pure oxygen fell in the same time from 150 to 113 millims. in diameter.

In forty-eight hours a balloon filled with hydrogen 154 millims. in diameter contracted to 87 millims., and then contained 250 cubic centims. gas, of which 53 cubic centims. were absorbed by pyrogallic acid and potash, showing the presence of 21·2 per cent. of oxygen, or sensibly the same proportion as in the external atmosphere.

If the upper end of a diffusimeter be closed by a thin sheet of rubber, and the instrument standing over mercury be filled with hydrogen gas, a contraction is observed to take place slowly, but to a greater extent ultimately than could be due to the diffusion of hydrogen as a gas. Beginning with 249 volume divisions of gas in the tube, the rise of the mercurial column, or reduction of volume, was 1·5 division in the first hour, 1·5 divi-

sion in the second hour, 2 in the third hour, 3 in the fourth hour, and 51 divisions in the first twenty-four hours taken together. Then the rise in the following successive days was 42, 59, 37, 29, 13, 5, 1, 0.5, 0.5 (in two days), and 0.0, the original volume of 249 volumes of hydrogen being finally replaced by 53 volumes of atmospheric air; barom. 747 millims., therm. 21° 1. The ultimate replacing volumes are here as 1 to 4.7. In gas-diffusion they are as 1 to 3.8.

A balloon filled with air subsided in forty-eight hours from 150 to 147 millims. in diameter, from the mechanical effect alone of the elasticity of the membrane in compressing the enclosed gas. These little balloons vary from 0.75 to 1 gm. in weight. Supposing the form to be truly spherical, a balloon of 150 millims. in diameter would have a surface of 0.0706 square metre (5.905 inches in diameter and 0.0844 square yard of surface). Supposing the balloon to be 1 gm. in weight, the thickness of the membrane will be  $\frac{1}{70.686}$  of a millim., with a specific gravity = 1, or  $\frac{1}{760.1}$  of a millim., with a specific gravity = 0.93, the admitted density of pure rubber. This last is a thickness of  $\frac{1}{1930.6}$  of an inch, or it would require nearly 2000 such films, laid upon each other, to form the thickness of a single inch. Yet such a film of rubber appears to have no porosity, and to resemble a film of liquid in its relation to gases—differing entirely in this respect from a thin sheet of paper, graphite, earthenware, or even gutta percha, as will appear hereafter. These last enumerated bodies appear all to be pervaded by open channels or pores, sufficiently wide to allow gases to be projected through by their own proper molecular movement of diffusion. But liquids and colloids have an unbroken texture, and afford no opportunity for gaseous diffusion. They form even in the thinnest film an impervious barrier to gas.

The penetration of rubber is much affected by temperature, and apparently in two different ways at the same time. An increase of temperature no doubt renders all gases less easily liquefied by pressure, and consequently less considerably absorbed by any liquid or colloid. But such an influence of heat appears to be counteracted in rubber by the tendency of that colloid to become more soft when heated, and to acquire more of liquid and less of solid properties. Certainly the rubber film becomes more and more permeable to gases as the temperature is elevated, within a moderate range. This was distinctly observed in operating with silk cloth varnished on one side with rubber, such as is sold as a waterproof material. Without anticipating a detail of the experiments, it may be stated in general terms that the same specimen of rubber was penetrated by air from the at-

mosphere passing into a vacuum, at the following rates per square metre of surface :—

At 4° C., by 0·56 cub. centim. of air in 1 minute.

At 14° C., by 2·25                         "                         "

At 60° C., by 6.63	"	"
--------------------	---	---

The volumes of gas are all reduced to barom. 760 millims. and therm. 20° C.

Such numbers are probably not strictly constant; for it appears that the effect of temperature upon rubber is much influenced by the length of time that the temperature is continued, the change in degree of softness with change of temperature requiring hours, or even days, fully to complete it. The rigidity of rubber under cold and its softening under warmth are well known to take place in a slow and gradual manner.

With the softening of rubber by heat, the *retentive* power of that substance for gases appears to be modified. Soft rubber, first charged with carbonic acid at 20°, and then made rigid by cold, appeared to lose its carbonic acid, when afterwards freely exposed to air, less rapidly than the same rubber equally charged but exposed from the first in its soft condition. The quantity of carbonic acid retained in the former case was 10·76 per cent., and in the latter 7·08 per cent. of the volume of the rubber, after a similar exposure of forty-eight hours. This point, although not sufficiently examined, is alluded to here on account of the analogy which appears to hold between rubber and the malleable metals in a power to absorb a gas when they are softened by heat, and to retain the same gas with great tenacity when they are afterwards made rigid by cold.

The condensation of oxygen gas by masses of solid rubber punched out of a block was made the subject of observation, by placing 50 grms. of that substance within a jar of oxygen standing over mercury during a period of several days. From the rubber afterwards there was extracted, by the action of a vacuum continued for twenty-one hours, 6.21 cub. centims. of gas; of which 3.67 cub. centims. were oxygen, 0.14 carbonic acid, and the remainder chiefly nitrogen. Taking the bulk of the rubber at 53.8 cub. centims., the oxygen absorbed amounts to 6.82 per cent. of the volume of the rubber. Oxygen then may be regarded as fully twice as soluble in rubber as the same gas is in water at the ordinary temperature. No experiment was made at a higher temperature; but as the penetrativeness of rubber is much increased by heat, the presumption is that the solubility of gases in rubber is increased in the same degree.

More than one attempt was made to identify the presence of free hydrogen in the substance of rubber after being kept in that



gas for some time, but with a negative result. The absorbed hydrogen may be too easily dissipated, owing to its extreme volatility.

*Dialytic separation of Oxygen from Atmospheric Air, (1) by means of other gases, (2) by means of a vacuum.*

1. A balloon of rubber filled with *hydrogen* and exposed to the atmosphere, gradually loses the former gas, which is finally replaced by a considerably smaller volume of air, presenting a deceptive resemblance to the diffusion of hydrogen gas into air. When the progress of the entrance of air was observed at different stages of the exchange, it appeared that after three hours, when the balloon had fallen from 150 to 128 millims. in diameter, the composition of its contents was—

Oxygen . . .	8.98	41.6
Nitrogen . . .	12.60	58.4
Hydrogen . . .	78.42	
	<hr/> 100.00	<hr/> 100.0

Setting aside therefore the hydrogen still remaining, the balloon now contained a portion of a mixture of oxygen and nitrogen in the proportion of 41.6 volumes of the former to 58.4 volumes of the latter. This was the largest proportion of oxygen to the nitrogen observed; for the former gas has a tendency to flow back again to the external atmosphere when the hydrogen becomes small in volume; and the proportion of oxygen becomes eventually no higher than 21 per cent. of the whole gases remaining in the balloon, including the hydrogen. Thus after six hours the proportion of oxygen was 33.63 to nitrogen 66.37 volumes, and after twenty-four hours oxygen 26.48 to nitrogen 73.52 volumes, the hydrogen constantly diminishing at the same time.

The entrance by infiltration of atmospheric air into a balloon of rubber inflated with *carbonic acid* gas brings us still nearer to a practical dialytic separation, as the carbonic acid can be withdrawn entirely by means of caustic alkali, after a certain time has elapsed, and the infiltrated air enriched with oxygen be dealt with by itself. A balloon containing carbonic acid, when placed in the atmosphere, was reduced in four hours from 160 to 90 millims. in diameter, and it had now acquired 199 cub. centims. of gas not dissolved by alkali. This gas was capable of reviving the combustion of wood burning without flame, and was found to consist of

Oxygen . . . .	37.1 vols.
Nitrogen . . . .	62.9 "
	<hr/> 100.0

To produce this concentration of oxygen, it is quite necessary that the operation be interrupted at an early stage, as was done in the last experiment; otherwise the oxygen diminishes again in proportion to the nitrogen, falling at last to the normal proportion of 21 per cent. as in the external air. Thus a balloon inflated by carbonic acid to 150 millims. in diameter, was found to lose nearly all its carbonic acid in the course of twenty-four hours. It gave 150 cub. centims. of gas after treatment with caustic potash. This was air of the composition,

Oxygen	.	.	.	.	.	22·6
Nitrogen	.	.	.	.	.	77·4
						<hr/> 100·0

and exhibited therefore no material augmentation in the proportion of oxygen.

It may be inferred from the familiar fact that air dissolved in water contains so high a proportion as 30 per cent. of oxygen, that if carbonic acid gas were divided from atmospheric air by a film of *water*, the former gas would come to be charged through the film with air bearing the same high proportion of 30 per cent. of oxygen. But it is not easy to imitate this experiment unless the dividing film is supported by a membrane of some sort. The air from the atmosphere, which entered a fresh ox-bladder preserved humid and inflated with carbonic acid, was found to possess 24·65 per cent. of oxygen to 75·35 of nitrogen, which is but a small increase in the proportion of oxygen. But the thickness of the membrane here was too great, and other circumstances of the experiment were unfavourable.

A balloon of rubber inflated to 150 millims. in diameter with carbonic acid was submerged in water, at 22° C., for forty-eight hours. Only a small portion of carbonic acid remained in the residual gas, which, after being washed with potash, consisted of

Oxygen	.	.	.	.	25·77
Nitrogen	.	.	.	.	74·23
					<hr/> 100·00

2. With the colloid septum properly supported, as by a stucco plate in the diffusiometer covered by a film of rubber (p. 403), a considerable separation of mixed gases can be effected. The constituents of atmospheric air appear to be carried through a film of rubber into a vacuum, nearly in the same relative proportion as the same gases penetrate singly (p. 405). The velocities of nitrogen and oxygen passing separately were observed to be as 1 to 2·556, and hence by calculation,

Oxygen	$21 \times 2.556 = 53.676$	.	.	40.46
Nitrogen	$79 \times 1 = 79$	.	.	59.54
				<hr/> 100.00

Hence air dialyzed by the rubber septum should consist of 40.46 oxygen and 59.54 nitrogen in 100 volumes. Now air from the atmosphere was found to enter the vacuum of the 48-inch diffusimeter-tube, through a disk of rubber 22 millims. in diameter, to the amount of 3.48 cub. centims. in twenty-one hours, under the pressure of the atmosphere; therm.  $23^{\circ}$  to  $24^{\circ}$  C. Of the 3.48 cub. centims. of gas so collected, 2 cub. centims. were absorbed by pyrogallie acid and potash, representing 42.53 *per cent.* of oxygen in the dialyzed air. Here the gas was transferred from the diffusimeter for examination by depressing the diffusimeter in mercury, and using a very narrow tube of rubber as a gas-siphon communicating between the gas in the diffusimeter and a jar inverted in the mercurial trough. The elastic tube is first filled with mercury, and, being of considerable length, a portion of it is drawn repeatedly through the fingers so as to throw the mercury and aspirated gas into the collecting receiver. The transference of gases in such circumstances may also be effected with much advantage by means of the vacuum-tube invented by Dr. Hermann Sprengel, as will immediately be shown.

The process of dialytic separation by means of a rubber septum may be varied in three points,—(1) in the condition of the rubber septum, which may be a film of rubber formed from caoutchouc varnish, as well as from distended sheet rubber; (2) in the nature of the support given to the septum, which may be a backing of cotton cloth or of silk (common waterproof cloth prepared by means of caoutchouc varnish, in short), as well as a plate of stucco, earthenware, or wood; and (3) in the means had recourse to for sustaining a vacuum, or at least a considerable degree of exhaustion, on one side of the dialytic septum, while atmospheric air, or any other gaseous mixture to be dialyzed, has access to the other side of the same septum. Or the air to be dialyzed may be compressed on one side of the septum, and left of the usual tension on the other side—inequality of tension on the two sides of the septum being all that is required to induce penetration.

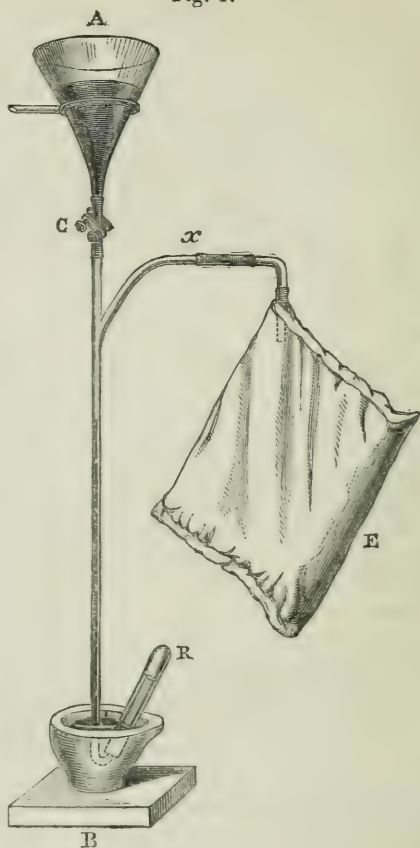
The pneumatic instrument of Dr. Sprengel (fig. 1) is peculiarly applicable to researches of the present kind. Indeed without the use of his invention some parts of the inquiry would have been practically impossible\*. The instrument was origi-

\* "Researches on the Vacuum," by Hermann Sprengel, Ph.D., Chemical Society's Journal, ser. 2, vol. iii. p. 9 (January 1865).

nally offered by the inventor as the means of producing a vacuum, or as an air-pump. But by bending the lower end of the straight fall-tube, the instrument may be further made to deliver gas into a receiver, and be used with advantage as the means of transferring small volumes of gas from one vessel to another.

While the mercury in the funnel A is allowed to flow downward into the barometer-tube CB, of  $2\frac{1}{2}$  millims. in diameter, by relaxing the clamp upon the adapter tube of rubber at C, a connexion is also made with the close receiver to be exhausted, such as an air-tight bag E, by means of the branch tube *x*. The air in E, gaining access to the Torricellian vacuum, is swept on by the falling mercury, and delivered below into the small gas-receiver R, previously filled with mercury and inverted over mercury in the mortar B below. The principal difficulty in obtaining a good vacuum in E by means of this apparatus arises from the necessity of joining the glass tubes in more than one place by means of adapter tubes of rubber. The directions given by Dr. Sprengel on this point require to be closely followed:—"The connexions between the glass tubes are made of well-fitting black vulcanized caoutchouc tubing, sold under the name of French tubing. This is free from metallic oxides, which render the tubing porous. Besides this all these joints are bound with coils of copper wire, which is easily accomplished with a pair of pliers." The joints should also be coated with gutta percha liquefied by heat, or with fused rubber. An exhausting-syringe, or air-pump,

Fig. 1.





may often be used with advantage to begin the exhaustion, and to withdraw the greater bulk of the air, if the receiver is large, the Sprengel tube being reserved to complete the exhaustion. The vacuum appears to be as perfect as can be formed in a barometer-tube filled with unboiled mercury, and to come within 1 millim. of the barometric gauge.

The following modifications of the experiment exhibit the dialytic action of caoutchouc in its various forms.

1. *India-rubber between double cotton cloth vulcanized.*

This was a common elastic carriage-bag 18 inches by 15. The surface of both sides amounted to 0.3482 square metre. The bag was pressed flat by the hands, and still further exhausted by means of Sprengel's tube. After all the contents of the bag were extracted and the collapse complete, the Sprengel tube began again to throw out air in a slow but exceedingly regular manner. A small portion of sawdust, or of sand, introduced beforehand into the bag, appeared to be useful in preventing the sides coming together too closely, but was not essential. The air thus extracted from the bag in one hour amounted to 15.65 cub. centims., or sensibly 1 cubic inch; therm.  $23^{\circ}$  to  $24^{\circ}$  C. Such dialyzed air, from three successive experiments of one hour each, contained 38, 40.3, and 41.2 per cent. of oxygen, the inferior proportion of oxygen in the earlier experiments being no doubt due to a small residue of undialyzed air remaining in the bag before exhaustion. This dialyzed air rekindled glowing wood, so as to illustrate the direct separation of oxygen gas from atmospheric air. For the purposes of combustion, it may be viewed as air from which one-half of the inert nitrogen has been withdrawn.

It will be convenient to express the permeability of the colloid septum with uniform reference to a square metre of area, and to an hour, or to a single minute of time. Here, for a square metre of cloth, the passage of air amounted to 44.95 cub. centims. (3 cubic inches nearly) per hour, or to 0.749 cub. centim. per minute.

The view which the observation suggests of the nature of such an air-tight fabric is, that it may be truly impenetrable to air when the composition and tension of the air are the same on both sides of the cloth; but it is penetrable when a vacuum or a reduced state of tension is maintained on one side of the cloth and not on the other. The compression of the air confined in a bag would no doubt have a similar effect, and then the flow would be in an outward direction. But there is no evidence of a porous structure in the varnished cloth. The gases of atmospheric air would pass through actual openings according to the law of

gaseous diffusion, which favours the nitrogen or lighter gas, while it is the oxygen which is found to pass through the material most readily in these experiments. The imbibition of the liquefied gas by the substance of the rubber, with the subsequent evaporation of this liquid into the vacuum on the other side, is all the explanation required.

## 2. *Vulcanized india-rubber tubing.*

A stout caoutchouc tube with an external diameter of 13 millims. (half an inch), an internal diameter of 9 millims., thickness of 2 millims., and length of 3·658 metres (4 yards) was exhausted, one end being closed and the other end connected with the Sprengel pump. The gas collected in thirteen hours amounted to 11·25 cub. centims.; therm.  $20^{\circ}$  to  $23^{\circ}$  C. This gas contained 37·8 per cent. of oxygen. The gaseous penetration is not great in so thick a tube, and there is reason to fear the influence of gaseous diffusion to a small extent. The admission of air would be equally sensible if the tube were occupied by coal-gas, or any other foreign gas, instead of being vacuous. As the inner surface of the tube amounted to 0·1034 square metre and the passage of air to 0·8653 cub. centim. per hour, the passage for a square metre would be 8·37 cub. centims. per hour, or 0·14 cub. centim. per minute. The rate of penetration through the tube-walls appears to be one-fifth of what was found for the rubber cloth.

## 3. *Sheet rubber, 1 millim. in thickness.*

Although an increased thickness was no doubt attended by slowness of passage, it was of interest to observe whether the proportion of oxygen per cent. might not at the same time be varied. The sheet used was still, however, as thin as the manufacturer could succeed in cutting from a solid cylinder of wrought rubber by the usual method. The rubber was not vulcanized. The sheet of rubber was made into a bag having 0·149 square metre (231 square inches) of surface, a double thickness of felted carpet being placed within the folds of rubber. A glass quill tube, cemented to the bag, communicated with the interior of the cavity, and was connected at the other end with Sprengel's tube. After the first exhaustion of the gaseous contents of the bag, for which the aid of an exhausting-syringe or air-pump is useful, air continued to infiltrate through the sheet rubber, but very slowly. Of the dialyzed air 11·45 cub. centims. were collected in four hours. This air contained 41·48 per cent. of oxygen, with a sensible trace of carbonic acid. The penetration for a square metre amounts to 19·2 cub. centims. of air per hour, or 0·32 cub. centim. per minute.

The same bag, left exhausted for eighteen hours, was found afterwards to yield at once 41.6 cub. centims. of air, containing 40.3 per cent. of oxygen, which had accumulated in the cavity of the bag; therm. about 20° C.

From a larger bag of similar thin sheet rubber, having a surface of 640 square inches, distended by ten or twelve ounces of sawdust, 21.35 cub. centims. of dialyzed air were obtained in one hour; barom. 761 millims., therm. 19°5 C. This dialyzed air appeared to consist of

Oxygen . . . . .	41.80
Carbonic acid . . . .	0.94
Nitrogen . . . . .	57.26
	<hr/> 100.00

It does not appear, then, that the increased thickness of the rubber septum tends to increase the proportion of oxygen in the dialyzed air, while this thickness causes the passage to be proportionally slower. The oxygen appears to attain, but never to exceed, at 20° C., the proportion of 41.6 to 58.4 nitrogen.

The thick rubber brings notably into view the carbonic acid of the air. The small proportion of this gas in air is probably increased in all experiments with the rubber septum, however thin. It was observed to rise so high in a small crowded room, as to negative the inflaming action of the oxygen on smouldering wood. But rubber appears to have a power to charge itself gradually from atmospheric air with about half per cent. of its volume of carbonic acid. This carbonic acid, accumulated in thick sheet rubber, appears again to be carried on by the other gases imbibed in a dialytic experiment.

#### 4. *Thin Balloons of india-rubber.*

These little balloons were made available for the dialytic passage of air into a vacuum by filling them with sifted sawdust through a funnel, an operation which requires some address. The balloon collapsed upon the sawdust, which formed an interior ball, the sides of rubber still retaining a thickness of about one-fiftieth of a millimetre. The rubber is not vulcanized. Such a ball, of which the original rubber weighed 0.76 gm., still remained 95 millims. in diameter after the air was exhausted. It was found, when exhausted, to admit 19.6 cub. centims. of dialyzed air in forty-one minutes (barom. 579 millims., and therm. 19° C.). The same air possessed 41.32 per cent. of oxygen. The ball had a surface of 0.0283 square metre, and it dialyzed 0.48 cub. centim. of air in one minute. For a square metre of surface this is a passage of 16.9 cub. centims. per minute. The passage therefore is about fifty times as fast as through a sheet of rubber



of 1 millim. in thickness, while the high proportion of oxygen is sensibly the same. Such a ball was found to dialyze air in the same manner for more than a month, if protected from mechanical injury.

Three such balls, each containing twenty-three ounces of sifted sawdust, were made to act together, by connecting them with three dependent branches from the same horizontal glass tube. The horizontal tube was connected at one end with an ordinary air-pump which produced a good vacuum by thirty or forty strokes of the piston. The other end of the horizontal glass tube was attached to a good Sprengel apparatus of the largest admissible size, constructed by Messrs. Elliot of the Strand. It was found, however, that the dialyzed air entered rather more rapidly than it could be extracted by a single Sprengel apparatus. This was at the rate of 5 cub. centims. in one minute; therm. about  $20^{\circ}$  C. The dialyzed air contained 40.5 per cent. of oxygen.

The greatest amount of aërial dialysis per square metre was obtained by means of a rubber bag, larger than usual, and weighing 1.55 gm. When filled with the sawdust and exhausted, this bag still remained of 143 millims. in diameter, and with a surface therefore of 0.0642 square metre. The air which passed through amounted to 17.05 cubic centims. in ten minutes; therm. about  $20^{\circ}$ . This air gave 40.7 per cent. of oxygen. For a square metre of surface, this is the passage of 26.5 cub. centims. per minute, the highest which has as yet been observed.

In the thin transparent envelope of the little balloon of rubber we have a colloid substance in the most favourable form yet applied to the dialysis of mixed gases. But there is still much room for improvement in the mode of using the thin septum in question. The balls are apt to contract considerably, owing to their elasticity, in the operation referred to, of filling them with sawdust; their walls become at the same time thicker and less quickly pervious. A mode of destroying the elasticity of the membrane when in its most attenuated condition, so that the balloon might be cut open and the membrane spread out without shrinking, would be very useful. Instead of depending upon the interior support of sawdust, the membrane could then be stretched over a more convenient frame to support it, of thin porous deal, of unglazed earthenware, and even of a felted fabric, or several thicknesses of unsized paper supported by a slight frame, so as to form a hollow cavity that admitted of being exhausted of air. The attention of manufacturers of rubber might be advantageously directed to the preparation and proper support of the thinnest possible septa of that material.

The varnish of rubber which appeared to offer the best septum on drying, was a thin solution of rubber in 200 times its weight



of chloroform. Four or five coats of this varnish required to be applied to a surface of wood, or of unglazed earthenware, to form an air-tight envelope. The film appeared to exceed in thickness the rubber balloons, and it dialyzed air less rapidly. But a better result may be expected at the hands of experienced manufacturers.

The thin rubber membrane of the balloons was stretched over the ends of glass tubes already closed with a plate of porous stucco—and also over the mouths of small glass bulbs or osmometers, closed with a disk of porous wood or of unglazed earthenware, and which presented a surface of one-hundredth of a square metre. The membrane of the balloon could only be applied while double; but after the covering was securely bound to the glass and cemented with fused gutta percha at the edges, the outer coating was torn off, so as to leave only a single thickness of rubber as the dialytic septum. A bulb of the kind described, when exhausted by a Sprengel pump, gave afterwards 16·36 cub. centims. of dialyzed air in two hours, containing by analysis 41·3 per cent. of oxygen, therm.  $23^{\circ}$  C.; in the following two hours, 17·35 cub. centims. of air, containing 42·6 per cent. of oxygen. This last is at the high rate, for a square metre of surface, of 14·46 cub. centims. per minute.

5. *Silk cloth varnished with rubber on one side, slightly vulcanized.*

This is a thin but close silk fabric, much used for waterproof garments. It appears also to be employed, when dyed of a fancy colour, in the preparation of artificial flowers and for other purposes. The silk cloth is of a single thickness; and the coating of rubber, which is of a black colour, appears on one side only. It is a much superior material to the ordinary cotton fabrics, which are double, with the two varnished sides pressed together, and is much more to be depended upon for being sound and free from pores than the "waterproof" cotton cloth. The silk cloth, however, should always be tested by examining air dialyzed by means of it. If the proportion of oxygen falls below 40 per cent., the silk is unsound at one or more spots. These spots may generally be discovered by wetting one side of the silk with a sponge and observing where the passage of water is indicated by a visible stain on the other side. The defective spot may be covered by a small disk of sheet rubber applied warm to the surface. Such varnished silk, although not the most rapid in its dialytic action, was more convenient in use than any other septum hitherto tried.

The varnished silk stretched over a disk of porous earthenware (for support) closing the mouth of the small glass bell-jar or osmometer, which has an opening of one hundredth part of a square metre, gave 10 cub. centims. of dialyzed air in one hour,

containing 42·2 per cent. of oxygen ; barom. 767 millims., therm. 23°·5. For a square metre of surface this is a passage of 2·77 cub. centims. of air per minute.

A small bag, useful for experimental purposes, was constructed of a portion of the same varnished silk, 0·53 metre in length by 0·27 metre in width, which had therefore a surface of 0·143 square metre. The varnished side was turned inwards. Between the folds of the silk was placed a double thickness of common felt carpet or a piece of wadding, so as to occupy the interior of the bag. A glass quill tube also entered the bag to the depth of a few inches, and projected as much outside, so as to admit of being connected, by means of a sound adapter tube of French rubber, with a Sprengel pump, as shown in fig. 1 (page 412). The edges of the silk cloth were cemented round by caoutchouc varnish, to a depth of 10 millims., so as to close the bag ; and care was taken also to cement the glass tube well to the edges of the bag. When the silk bag is exhausted of air, it remains nearly flat, and feels hard like a piece of cardboard. Such an *air-dialyzer* is further improved by interposing a strong glass flask or bottle, of one or two litres in capacity, between the bag and the pump, so that both are exhausted of air at the same time. The flask must be strong enough to bear the full pressure of the atmosphere without breaking. An auxiliary air-pump, to produce the first exhaustion, cannot well be dispensed with where the space to be made vacuous is so considerable ; the Sprengel tube is brought into action afterwards. The advantage gained by the vacuous flask, and even by the thick wadding placed within the bag, is that they form a magazine in which the dialyzed air can be allowed to accumulate for several hours or a whole day, and from which the air may afterwards be drawn quickly by the Sprengel tube for the purpose of experiment. A narrow glass receiver tube, which can be closed by the thumb, may be used to take 5 or 6 cub. centims. for an observation on the inflammation of a chip of wood in the highly oxygenated air. When the proportion of oxygen is under 33 per cent. the wood is not rekindled ; but in the ordinary action of this dialyzer the oxygen is seldom found under 40 per cent. The best result is obtained when the exhaustion is within half an inch of the barometric vacuum. When the pressure was allowed to fall to one-half or one-third of an atmosphere, the proportion of oxygen was lessened by 2 or 3 per cent.

The action of heat and cold on the penetrability of rubber is considerable, as has already been stated. Operating with the dialyzing-bag described, without any intermediate flask, the volume of air collected in twenty minutes was 6·35 and 6·57 cub. centims. in two consecutive experiments ; barom. 760 millims.,

therm.  $20^{\circ}$ . For a square metre the rate is 2.22 and 2.29, average 2.25 cub. centims. per minute. The proportion of oxygen was, in the first experiment 42.5, and in the second 41.66 per cent.

When the same dialyzing-bag was kept at a temperature of  $60^{\circ}$  C., the volume of air collected in seven minutes was 6.22 and 7.06 cub. centims. For the square metre this amounts to 6.21 and 7.05, mean 6.65 cub. centims. per minute. The passage of air through rubber is therefore almost exactly three times as quick at  $60^{\circ}$  as at  $20^{\circ}$  C.

Again, the dialyzing-bag was kept at  $4^{\circ}$  C. by being surrounded by ice and salt. The air now collected in seventy-two minutes was 5.78 and 5.77 cub. centims. in volume—for a square metre, 0.56 cub. centim. per minute. The passage of air through rubber thus appears to be four times as slow at  $4^{\circ}$  C. as it is at  $20^{\circ}$ . The proportion of oxygen in the dialyzed air increased at the same time. In the two portions of air collected at  $4^{\circ}$  the oxygen was 46.75 and 47.43 per cent. The increase of oxygen at a low temperature was confirmed in other experiments; but it appeared at the same time that the rubber was liable to acquire a true porosity to a slight extent when retained for some hours about  $0^{\circ}$  C. The rubber then allowed air to pass through it containing no more than 28 or even 23 per cent. of oxygen, and in volume still very small. The rubber has become rigid by the cold, and is now acting feebly as a porous substance, allowing a little gas-diffusion to take place through its substance. Such a condition, which is accidental to caoutchouc at a low temperature, appears to be constant with gutta percha, a harder material, at  $20^{\circ}$  C., and even higher temperatures.

A large bag of varnished silk with a surface of 1.672 square metre (two square yards) was found still more convenient. It was, however, rather beyond the exhausting-power of the largest Sprengel-pump. It yielded in eight minutes, without any collecting-flask, 22, 21.55, and 21.5, mean 21.68 cub. centims. This was a supply of 2.71 cub. centims. per minute, and was at the rate, for a square metre, of 1.62 cub. centim. per minute. The supply would have been about a half more if the dialyzed air had not gained upon the pump. The air of the first and last observations contained respectively 41.89 and 41.85 per cent. of oxygen.

The usual proportion of oxygen in air dialyzed by rubber appears to be about 41.6 per cent.; and it may be described as atmospheric air deprived of one-half of its usual proportion of nitrogen. A single dialysis of air therefore carries the experimenter already halfway from air to pure oxygen as the final result. But the gain by a second dialysis could not be so great,



as it would only withdraw one-half of the nitrogen that remained after the first operation, a third dialysis one-half of the nitrogen remaining after the second operation, and so on—each step of the concentration of the oxygen being obtained at a greater cost than the last, and the best conceivable result being only a good approximation. The practical problem which is suggested by the air-dialyzer is, to attain the means on a large scale of reducing to one-half, or so, the proportion of nitrogen in atmospheric air, to be applied to certain useful purposes.

#### 6. *Percolation of air through gutta percha and other septa.*

Thin transparent sheets of a certain material represented as air- and water-tight are in common use. It is often spoken of as consisting of caoutchouc, but appears to have a body of gutta percha, softened probably by a drying-oil. From its softness and thinness, this sheet of gutta percha appeared at first highly promising. But it appears not to be free from small apertures for any considerable surface. When a small sound portion was operated upon, air was found to percolate through it very slowly. In a tube diffusimeter of 1·3 metre in length and 20 millims. in diameter, closed at the top with this septum supported by stucco, the mercurial column fell from 28·7 to 22·625 inches in 18½ hours. The gas which had entered above the mercury measured 13·54 cub. centims., and was found to contain 20·2 oxygen to 79·8 nitrogen—a proof that the air had entered by gas-diffusion. The material is in fact of sufficient porosity to permit the molecular passage of gases in a slow manner.

Varnishes of gelatine and of drying-oil have been tried as dialytic septa, but hitherto without marked results.

[To be continued.]

#### LVI. *Note on Change of State as affecting Communication of Heat.* By JOSEPH GILL, Esq.\*

**B**Y a train of analogies of a kind not admissible by our Baconian system of philosophy, an Aristotle or a Kepler might have dreamed of some physical law in virtue of which *matter in a lower state cannot, by direct contact, communicate heat to matter of the same kind in a higher state though at a lower temperature.* For instance, ice at 32° cannot communicate heat by direct contact to water overcooled to a lower temperature; and water under atmospheric pressure heated above its normal boiling-point, which, under certain conditions, may easily be done, cannot impart heat by direct contact to steam at the lower

\* Communicated by the Author.



temperature of  $212^{\circ}$ . In the former case the contact of ice with overcooled water determines an instantaneous congelation of part of the water with a rise of temperature to  $32^{\circ}$ ; and in the latter case the contact of steam at  $212^{\circ}$  causes a sudden ebullition of the overheated water, with a fall of temperature to  $212^{\circ}$ , and so of analogous experiments with other substances. This, by the old school, might have been taken as a kind of negative proof, —a repugnance on the part of Nature to permit an approach towards the inversion or suspension of a physical law. The immediate cause of the phenomena has been referred by modern investigators to molecular conditions and polar influences in the ultimate particles of matter; and as long as the phenomena were confined to circumstances like those mentioned above, we might perhaps rest satisfied with such explanation. But in the case of aqueous solutions there appears to be something like a more positive proof of the above imagined law.

A saturated solution of common salt in water boils, under atmospheric pressure, at  $226^{\circ}$ , and yet the steam which it emits is only  $212^{\circ}$ ; and so also of other solutions which boil at temperatures even beyond  $270^{\circ}$ . It is well known that though the presence in a liquid of a substance dissolved in it may, to a considerable amount, raise the temperature at which the liquid boils under a given pressure, yet, unless the dissolved substance enters into the composition of the vapour, the relation between the temperature and pressure of saturation of the latter remains unchanged. It is not difficult to conceive that the affinity or attractive influence between the particles of the water and those of the dissolved body should hold down the water-particles in close association with the solid particles against the force of heat tending to separate them, and that thus the boiling-point of the solution should be raised; but it is not so easy to conceive why the steam-bubbles rising from the bottom of a mass of a solution of potash boiling at  $272^{\circ}$  should escape from the surface as saturated steam of  $212^{\circ}$  without any indication of having been superheated by contact with the liquid  $60^{\circ}$  hotter, and by radiation during their transit through this liquid from the bottom to the surface. It seems very probable that, as supposed by Regnault, molecularly each particle of steam is formed as saturated steam at a pressure actually corresponding to the temperature of the boiling liquid, the chemical attraction of the dissolved salt coercing it in the same manner as it holds down the particles of water against the act of boiling through a thermometric range of  $60^{\circ}$  in the case under consideration (from  $212^{\circ}$  to  $272^{\circ}$ ); but when a number of steam-particles coalesce to form a bubble, it is reasonable to suppose that the smallest visible steam-bubble must be of enormous dimensions

compared with each individual steam-particle which enters into its composition, and that the sphere of chemical attraction of the salt cannot penetrate far into the interior of the spherical mass of steam forming a visible bubble. Consequently it may be supposed that a steam-bubble of a given weight formed at the bottom of the solution should assume a size very nearly equal to that of a steam-bubble of equal weight formed in pure water boiling under the same pressure; and, unless there be some *special reason why steam should not be superheated by passing through an aqueous solution considerably hotter than itself*, it might be expected that the steam-bubbles formed at the bottom of a mass of a solution of potash or muriate of lime at a temperature of upwards of  $270^{\circ}$  under atmospheric pressure would show some sign of having acquired a temperature somewhat above  $212^{\circ}$  in their passage from the bottom to the surface of the liquid. The general accuracy of Regnault's experimental researches is universally admitted; and his experiments have fully proved the fact enounced by Rudberg long ago, that the steam from aqueous solutions boiling at temperatures above  $212^{\circ}$  is still only  $212^{\circ}$ . At the same time I think it will be admitted that Regnault's explanation of the phenomena, though applicable molecularly, does not satisfactorily apply to the passage of visible steam-bubbles through an aqueous solution much hotter than the normal boiling-point of pure water under a given pressure. The subject seems to be still enveloped in obscurity, and requires further investigation.

Palermo, October 13, 1866.

LVII. *On the Freezing of Water at Temperatures lower than  $32^{\circ}$  F.*  
By ARTHUR HILL CURTIS, LL.D., *Professor of Natural Philosophy in the Queen's University*.\*

WHEN water which has been reduced in temperature below the ordinary freezing-point without becoming solidified is agitated, it is well known that a portion of it becomes frozen; and the question immediately arises, how much? This question has been already answered, and the result arrived at tested by experiment. In obtaining the result, however, it has been assumed that *all* the ice is formed either at the temperature of  $32^{\circ}$  F., or at the initial temperature of the water. Now a little consideration will show that neither of these assumptions is true. The congelation commences at some one point, or at a certain finite number of points; certain small par-

\* Communicated by the Author.

ticles of ice are formed at these centres of congelation, a large quantity of heat is given out by each particle, and as water is a bad conductor of heat, this is principally communicated to the *adjacent* particles of water, and when immediately afterwards these particles pass from the liquid to the solid state, this transition takes place at a temperature higher than the initial one. For a similar reason the liquid particles adjacent to these last pass into the solid state at a temperature still higher; and thus the process continues until, at last, all the ice formed and the surrounding water are raised to the temperature of  $32^{\circ}$  F. The process of course would terminate here if the vessel containing the liquid were a perfect non-conductor of heat, but as this condition is unattainable, the *reduced value* in water of the vessel must be found, and this included in the given quantity of water.

As the consecutive portions of ice are formed at different temperatures varying according to a complicated law, which depends on the conductivity of water, its latent heat, and the specific heat of ice, the exact determination of the quantity of ice formed would at first sight appear to be of considerable difficulty; this difficulty, however, as I shall presently show, is only apparent.

Before proceeding to the consideration of the problem itself I shall establish the following theorem:—

If  $\lambda_1$  denote the latent heat of water at the temperature  $32^{\circ}-t_1^{\circ}$ ,  $\lambda$  the latent heat of water at  $32^{\circ}$ , and  $c_1$  the mean specific heat of ice at the temperature  $32^{\circ}-t_1^{\circ}$ , then

$$\lambda_1 = \lambda - (1 - c_1)t_1.$$

To prove this, consider one pound weight of water at the temperature  $32^{\circ}-t_1^{\circ}$ , and suppose it (1) converted into ice at the same temperature, then (2) raised as ice in temperature to  $32^{\circ}$ , then (3) converted into water at  $32^{\circ}$ , and finally (4) cooled down again as water to  $32^{\circ}-t_1^{\circ}$ , and consequently brought back to its original state. Now since the quantity of heat latent and sensible in the pound of water is the same at the commencement and end of the process, it is evident that the sum of the two quantities given out by it in the stages (1) and (4) must be equal to the sum of those communicated to it in the stages (2) and (3). This consideration at once gives the equation

$$\lambda_1 + t_1 = \lambda + c_1 t_1, \text{ or } \lambda_1 = \lambda - (1 - c_1)t_1. \quad (1)$$

It may be remarked that no assumption is here made about the specific heat of ice being constant for different temperatures;  $c_1 t_1$  is in fact only a symbol for the entire quantity of heat necessary to raise one pound weight of ice from  $32^{\circ}-t_1^{\circ}$  to  $32^{\circ}$ .

This being established, I shall now proceed to consider the

question proposed. Let  $W$  denote the weight in pounds of the given quantity of water inclusive of the containing vessel reduced,  $32^\circ - t^\circ$  its temperature, and  $Q$  the weight of the ice formed; let  $q_1$  denote the weight of any particle of ice,  $t_1$  the temperature at which it was formed,  $\lambda, \lambda_1, c_1$  being as above; let  $q_2, t_2, \lambda_2, c_2$  be similarly related to a second particle,  $q_3, t_3, \lambda_3, c_3$  to a third, and so on; then, as  $q_1, q_2, \&c.$  are respectively heated as water through  $t^\circ - t_1^\circ, t^\circ - t_2^\circ, \&c.$ , and as ice through  $t_1^\circ, t_2^\circ, \&c.$ , while  $W - (q_1 + q_2 + q_3 + \&c.)$  is heated as water through  $t^\circ$ , by equating the quantity of latent heat rendered sensible to the quantity of heat spent in raising the temperature of the whole we obtain the following equation:—

$$\lambda_1 q_1 + \lambda_2 q_2 + \lambda_3 q_3 + \&c. = t(W - q_1 - q_2 - q_3 - \&c.) + q_1(t - t_1) + q_2(t - t_2) + q_3(t - t_3) + \&c. + c_1 q_1 t_1 + c_2 q_2 t_2 + c_3 q_3 t_3 + \&c.$$

Or substituting for  $\lambda_1, \lambda - (1 - c_1)t_1$ , for  $\lambda_2, \lambda - (1 - c_2)t_2$ , and similarly for  $\lambda_3, \&c.$ , we obtain

$$\lambda(q_1 + q_2 + q_3 + \&c.) = tW,$$

or

$$\lambda Q = tW.$$

If we denote by  $x$  the ratio of  $Q$  to  $W$ , we have

$$x = \frac{t}{\lambda}.$$

The quantity which is here denoted by  $\lambda$  is the number of units of heat requisite to convert a pound of ice at the temperature of  $32^\circ$  F. into a pound of water at the same temperature, the *unit* of heat being that quantity which is sufficient to raise the temperature of a pound of water through  $1^\circ$  F. The value of  $\lambda$ , according to the experiments of Provostaye, Desains, and Reg-

nault, is 142.65; so that  $x = \frac{t}{142.65}$ . If instead of measuring

change of temperature by the Fahrenheit scale we employ the Centigrade, and define the unit of heat to be the quantity of heat requisite to raise a pound of water through  $1^\circ$  of that scale,

we have  $x = \frac{\theta}{79.25}$ , where  $-\theta^\circ$  denotes the temperature of the water in its initial state, as determined by the Centigrade thermometer. If we adopt the measure of the latent heat of ice at  $32^\circ$  F., or zero Cent., deduced from the experiments of Person,

the above expressions will become  $\frac{t}{144}$  and  $\frac{\theta}{80}$  respectively.



LVIII. *Remarks suggesting doubts respecting the received value of  $\mu$ , the Index of Refraction of the Lens.* By ROBERT TEMPLETON, Esq.\*

[With a Plate.]

1. A SERIES of very small holes being perforated in a thin sheet of brass in a gradation of sizes varying from about one-tenth of a millimetre to about fifteen tenths of a millimetre in diameter, if minute dots on a slip of cardboard be examined through them, a set of measurements can be taken of the distances at which the most perfect vision of the dots is obtained. A few trials will be required with an unpractised eye, as the observer does not at first feel quite sure at what distance the object is best seen; but very soon a set will be obtained such as is contained in the third column of the annexed Table:—

No.	$\delta$ .	D.	Log $\frac{\delta}{D}$ .
	millim.	millims.	
1	·15	28	7·7289
2	·25	43	7·7644
3	·32	63	7·7059
4	·55	102	7·7318
5	·81	150	7·7324
6	1·00	165	7·7825
7	1·07	190	7·7506
8	1·52	260	7·7668

2. The measurements in this column are a single set, taken in a well-lighted room, at a time when the sun was high but not shining into the room. As far as has been observed, they are constant for the same degree of light†.

3. The diameters of the small holes given in the second column being divided by the distances corresponding to them in the third, the logarithms of the quotients are placed opposite to them in the fourth column. These logarithms are perceived to be as nearly constant as can be expected, it being somewhat difficult to settle upon the precise point of perfect vision within a certain range of tolerably distinct vision; but the smaller the dot, consistent with exact definition, the more readily is the exact distance of perfect vision determined. We find, then, that for each hole there is a distance of quite perfect vision, a nearer or

\* Communicated by the Author.

† Some of the experiments here repeated were made many years ago, in an attempt to show that the adaptation of the eye to vision at different distances could only doubtfully be attributed to an exercise of muscular power, since a limit ought to be arrived at, at which the effort to maintain vision would cause it to become more or less intermitting.

further distance of more or less distinct vision, gradually dissolving into a diffused glare.

4. With larger holes it is not so easy to fix on the exact point ; but it may be remarked that with all eyes there is a point where exact definition ceases ; it is usually at about one and a half to two and a half metres from the eye.

5. The mean of the above logarithms is 7.7454, corresponding to an angle of  $19' 8''$  ; and it may reasonably be assumed that in a constant light the hole invariably subtends, at the dot or other object looked at, such angle when the dot or object is perfectly well seen.

6. If the pupil be dilated with belladonna, extraneous light carefully excluded, the other eye closed, and the experiment again tried, vision is found to be perfectly restored with any one hole at the distance corresponding to that hole.

7. When the edge of a little fragment of silvered glass is brought up to the eye (that is, held at about 10 to 15 centimetres from it), so that the pupil can be examined while the eye runs along a vista of objects, it will be found that the eye can be brought to bear on an object at any particular distance without distinct vision occurring, unless the act be accompanied by volition ; but the moment the mind wills to see the object, the iris obeys the impulse, contracts or expands as the case may be, and the object is clearly seen. There is a noticeable interval between the exercise of the will and the movement of the iris. The iris would seem to exercise no influence on vision further than mechanically controlling the brightness of the spectrum on the retina.

8. If a finger be held up between the eye and the landscape in the background and steadily looked at with one eye, the landscape is not lost sight of, though not definitely seen ; parallel rays, therefore, as well as those diverging from the finger, are impressed upon the retina at the same moment ; yet the difference of foci under these circumstances is fully a millimetre. The depth of the rods and bulbs (the sentient portion of the retina) is, however, only .014 millim. or thereabouts.

9. It has been shown that, within ordinary reading-distance, in a good light, from any point of an object a conical pencil of rays, the vertical angle of the cone being  $19' 8''$ \*, falls upon the cornea and is transmitted through the eye, undergoing therein refractions which bring the rays of which the pencil is composed to a focus behind the lens. If the focus for parallel rays be imagined to be at the retina, it is utterly impossible that the focus for these rays of a conical pencil can ever be so near as the

\* That is, more or less, varying with the individual and the light.

retina; the focus will be further and further removed the nearer the object is approached to the eye.

10. When the human lens has been removed by the operation of couching, the person operated on has sight so far restored that he can go about\*, distinguish clearly light from shade, and be conscious of the presence of obstacles. We can realize the condition of such persons by placing before the eye a glass lens of 50 to 100 millims. negative focus; by, however, interposing a small hole (Nos. 2, 3, or 4 of preceding Table) in a sheet of brass between the glass and the eye, vision is perfectly restored, though for obvious reasons the objects regarded appear faint. In these circumstances the focus of rays from a distant object is far beyond the retina.

11. Tracing into the eye an exterior ray of one of these conical pencils (that is, one making an angle of  $9' 34''$  with the axis of the eye), we find it come to a focus at a distance behind 22.2 millims., the distance from the cornea we have assumed for the focus of parallel rays—that is, for the retina. Under  $f'''$  in the annexed Table are given these focal distances for each of the experimental holes.

Nos.	$f'''$ .	$\epsilon$ .	$\phi$ .	$\epsilon \tan \phi$ .
	millims.	millims.		millim.
1	42.94	20.74	6 46	.041
2	31.36	9.16	15 22.7	.041
3	28.80	6.60	21 24	.041
4	25.65	3.45	41 11.8	.041
5	24.45	2.25	63 33.1	.042
6	24.00	1.80	79 50.5	.042
7	23.88	1.68	85 51.2	.042
8	23.70	1.17	124 22.6	.042

12. Subtracting 22.2 millims. from these several values of  $f'''$ , we have the quantities in the adjoining column under  $\epsilon$ . These are the distances at which the foci are respectively formed in rear of the retina. In the fourth column we have the angle which the exterior refracted ray of each pencil makes with the axis.

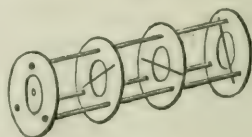
13. Taking the first, or any of these values of  $\epsilon$ , and multiplying it by the tangent of the angle ( $\phi$ ) corresponding to it, we have approximately the radius of the minute disk formed on the retina by the collective light of each pencil. Curiously enough, this value (.041 millim.) is much about the same quantity given above for the depth of the perceptive layer of the retina.

\* *Vide* Philosophical Transactions, 1801, p. 66.

14. The human lens, owing to its being less refractive, is far the best to experiment on; but none being procurable, many experiments were made on ox-eyes to determine the position of the focus of parallel rays. The eyes vary much in dimensions, and therefore require the radii and distances to be carefully measured in each case of trial; the position of the focus varies also, in water from 40 to 48 millims. from the rear of the lens. The best observation in a medium-sized eye gave 44 millims. In air the focus would appear to be at 6 millims.; but there is great difficulty in measuring it; it is consequently doubtful. While the lens was in the water, the diaphragm which transmitted the parallel rays was shifted over different parts of the lens within a small compass; but the focus appeared to undergo no alteration thereby.

15. Assuming that the aqueous and vitreous humours have in the ox-eye the same refractive indices as in the human eye, calculation gives 1.5066\* for the index of refraction of the ox-eye lens, and the focus for parallel rays entering the cornea is found to be 37.2 millims. from the back of the lens, or exactly 4 millims. more than the measured distance from the back of the lens to the retina. The air-focus gives a somewhat higher refractive index, supporting the opinion that the central parts of the lens have a higher refractive power, since its focus was almost exclusively of rays which passed direct through the centre, a small diaphragm having been used. These results are not entitled to any particular confidence.

16. From what has been stated above, it would appear to follow that all that the retina requires for distinct vision is a certain amount of illumination on a certain-sized but minute disk of its surface,—and, if so, that the eye is at all times prepared for vision at every distance, the size of the pupil determining what that distance shall be. To test this, a little frame was constructed to carry four diaphragms on the same imaginary axis and parallel to each other: to the first a small piece of sheet-brass was affixed, in which, commanding the centres of the diaphragms, some small holes were pierced, all within a space not larger than the pupil,—the central hole just large enough for accurate vision of distant objects; the others such as are, in



\* Dr. Wollaston has ascertained the refraction out of air into the centre of the recent crystalline of oxen and sheep to be nearly as 143 to 100, into the crystalline of fish and into the dried crystalline of sheep as 152 to 100." —Dr. Young's "Lecture on the Mechanism of the Eye," Phil. Trans. 1801, p. 42.



the preceding Tables, numbered 1, 2, 3. The other three diaphragms having threads stretched across them, were placed at distances corresponding to the diameters of the holes. Bringing the brass plate up to the pupil of the eye so that all the holes could be seen through at once, it was satisfactorily determined that each thread could be seen distinctly at the same moment with a church at a considerable distance, not by successive fiftful glances, but all steadily and sharply discernible at the self-same moment,—none, besides, seen distinctly (as was subsequently ascertained), except through its own hole and at its own particular distance\*.

17. It will be gathered from the preceding remarks, that there are questions relating to the phenomena of vision open to still further investigation—that facts are wanted which can only be obtained by most delicate experiments and carefully conducted observations. It may, in truth, be said that nothing whatever has been done to make us better acquainted than we were half a century ago with the refractive densities of the humours,—one value at the present moment being only guessed at, assumed, to satisfy previously adopted notions†. The law of decrease of the

\* It follows as a corollary from this, that in the case of persons with presbyopic eyes, if a horizontal row of some half-dozen holes  $\frac{1}{4}$  millim. in diameter be pierced in a narrow sheet of brass at distances of  $1\frac{3}{4}$  to 2 millims. from each other, and a similar set in the same line for the other eye, the lower edge of the little sheet of brass being curved to suit the contour of the face, bringing this close up to the eyes, vision at ordinary distance is so restored that the experimenter can read with tolerable facility; and that this is not due, as might be argued, to excluding all but parallel rays, is readily determined by using holes of sizes suited to other distances.

When the pupil of the presbyopic eye is diminished by inserting beneath the lid paper prepared with the Obi bean (*Phytostigma venenosa*), vision at short distance is restored. The effect does not last long, and is somewhat impeded by the lachrymation which accompanies the use of the paper; but of the fact there can be no doubt.

† “It is not my intention to subject anew to criticism the long series of incorrect views on the subject. I am not writing a history of errors. We now know what change the dioptric system undergoes in accommodation; and the source of this knowledge alone can be here sketched in its leading features. *The change consists in an alteration of form of the lens; above all, its anterior surface becomes more convex and approaches to the cornea.*” —F. C. Donders, ‘On Accommodation and Refraction of the Eye,’ Translation, p. 10.

“It was not until after direct proofs (within reach of every one’s observation and comprehension) of the change of form of the lens had been brought forward by others that Helmholtz placed the able investigation of Thomas Young in its proper light.”—*Op. cit.* p. 11.

“The subject is one of importance; for it is only by taking this higher index of refraction into account that we get rid of the paradoxical result that, in a well-formed eye, parallel incident rays should be brought to a focus behind the retina. The coefficient of refraction is now fixed by Listing at 1.455.”—*Op. cit.* p. 39.

value of  $\mu$  from the centre of the lens to the surface is quite unknown\*, the form of the caustic of refraction, as it really exists, quite untraced; we are hence unable to form the slightest conjectures in explanation of the diversified forms of the eye in the lower animals, or of the extraordinary variety in the comparative distances of the arched surfaces from each other, and that, too, under circumstances in which no reason can apparently be assigned why they should not be as identical in form and position as they are similar in function.

18. The curvatures which generate these surfaces are so nearly circular ares, in those portions at least which receive, or through which pass the rays of light, that the eye, armed with powerful glasses, can detect no deviation from perfect conformity; yet it may readily be accepted that they are not so simply curved. What, then, is their form? and what also are the modifications which the index of refraction undergoes as we proceed from order to order, and family to family, in the brute creation?

19. We find in the human eye† the retina comparatively far distant from the back of the lens, and with a radius of curvature about half the entire horizontal axis; in the elephant, with a lens not much differing in form, the retina is half as close again to the lens, and the radius of curvature considerably greater than the entire axis. Is the value of  $\mu$ , then, in this latter case, so very much greater than in the human eye? or what can be its law of decrease that will admit of a caustic of refraction of such unwonted flatness? a flatness with nothing like it, as far as is known, except in the whale (*Balæna Mysticetus*), in which likewise the centre of curvature is in front of the cornea.

20. In *Squalus Acanthias* and *Hystrix cristata*, creatures differing entirely in habit from each other, the eyes scarcely differ

\* Assuming the curvatures to be ares of circles, if  $z$  be the arc measured along the curvature of the cornea from its centre (or point traversed by the axis of the eye), and  $\mu$  the index of refraction of the lens, then the value of  $\mu$  for values of  $z$  up to  $30^\circ$  (corresponding to the largest size of the pupil) will be tolerably well represented by  $\log \mu = \cdot 16555 - \cdot 0020434 \sin^2 \cdot 55z$ . On the other hand, if the curvatures be generated by parabolas differing insensibly from circular ares, a constant value of  $\mu$  ( $1\cdot4388$ ) will convey the refracted rays into a focus at the retina, at least with 4-figure logarithms; but making the subnormals vary a little with  $\sin z$ , any degree of precision required can be attained. The change of value of  $\mu$  involved in the case of circular ares is very great, far beyond the limits of probability; we may more reasonably suppose it intermediate betwixt the conditions indicated above; but we really know nothing about it.

† Vide Detmar Wilhelm Sæmmering *de Oculorum Hominis Animaliumque Sectione horizontali Commentatio*. In the comparisons instituted in the text, the distance from the cornea along the axis to the rear of the lens (including all the refracting surfaces) is assumed equal to 10. (See also *infra*, p. 432.)

in form or in comparative dimensions, the lens nearly globular in each, yet the retina is excessively close to the lens in each, twice as close as it is in the cod's eye, and nearly three times as close as it is in the sturgeon's; is, then, the value of  $\mu$  so great, globular though the lenses be, as would be required should the rays come to a focus on these little-distant retinas?

21. *Testudo Mydas* and the crocodile (*Crocodilus sclerops*) have the cornea and lens closely approximating in form; however, the retina in the former is twice as distant, and its radius of curvature twice as great.

22. These comparisons could easily be multiplied, and most singular differences shown to exist in even closely allied families. It is quite possible to imagine that the conformation of the animal and the mode of life allotted to it may demand very essential differences in the sizes and proportional distances of the various parts of the eye; still that the refractive densities of the humours should be subjected to the marvellous diversity required to account for differences of comparative distance from lens to retina of from 19 to 3, and of lengths of radii of curvature from 21 to little more than one-third that quantity, is not exactly what would be expected.

23. Would it be possible to make the eye tell its own tale? There being little difference in the refractive indices of water and of ice, it might possibly not vitiate the results if freezing were had recourse to; at any rate introduced error could be determined and allowed for; and the experiment, if successfully tried in regard to the human eye, the ox-eye, and the cod's, would enable us to escape many an error likely to arise from a sole consideration of the phenomena of vision as it occurs in man.

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The accompanying Plate, illustrative of the forms of the refracting surfaces, &c., in the eyes of animals, and the following Table are extracted from the work of Detmar Wilhelm Sæmmering *de Oculorum Hominis Animaliumque Sectione horizontali Commentatio*.

#### EXPLANATION OF PLATE VI.

Fine concentric lines were traced on a plate of glass at distances of 1 millimetre from each other, beginning with 3 millims. radius and ending with 35. The plate of glass was then placed over the figures in the younger Sæmmering's work, and the curvatures, when accurately adjusted, read off. The distances of the surfaces were likewise read off. The numbers so read off were next reduced to a common relation of 10 millims., from the first refracting surface to the last, for the purpose of comparison, and are in this state figured in the Plate.

	6.3	8.6	5.7	10.3
Puella.....	0	3.6	7.3	21.4
	6.5	8.0	4.2	9
Simia Inuus .....	0	3.6	8	18.4
	6	4	3	8
Marmota alpina.....	0	2.5	7.3	12.7
	6.3	3.7	3.5	7
Hystrix cristata.....	0	2.6	8.5	11
	11.2	9	7	14
Didelphis gigantea .....	0	4.8	14.9	23.8
	5.7	4	4.8	7.5
Ursus Lotor .....	0	2.5	8.3	12
	9.5	7.3	8	13
Canis Lupus .....	0	6.3	15.5	21
	11.3	8.8	10.2	15.5
Felis Lynx .....	0	7.5	18.8	28
	16.4	12.2	10.7	30
Equus Caballus .....	0	6.5	20.2	39
	13	9	7.5	16.7
Antilope rupricapra .....	0	5.1	17.5	26.4
	14.8	10.5	8.0	29.8
Elephas asiaticus .....	0	6.5	13.9	25.5
	5.3	4	3.5	5.6
Castor Fiber .....	0	2.2	6.7	10.8
	13.5	6.3	6.0	19
Phoca groenlandica .....	0	3.7	14.6	27
	16.5	11.8	9.8	28.5
Balæna Mysticetus .....	0	6.4	18.4	28.3
	8.5	10	9	19.6
Falco Chrysaetos .....	0	6.4	14.8	31.3
	12.5	10	9.2	25.5
Strix Bubo .....	0	7.5	22.2	38.3
	5.6	4.5	3.4	9.8
Psittacus Aracanga .....	0	3.6	8	14.7
	10.8	13.3	9	22
Struthio Camelus .....	0	8.7	19.6	39
	6.4	5	4	13
Anas Cygnus .....	0	2.4	9.3	15
	6.2	2.3	2.1	12.0
Testudo Mydas .....	0	2	6.3	15.3
	6.2	4.5	4.0	9
Crocodylus sclerops .....	0	2.6	8.9	14.2
	3.7	4.6	3	6.5
Lacerta Monitor .....	0	1.4	5.4	8.8
	17	4.4	4.4	10.6
Raja clavata .....	0	1.4	10.2	14.6
	7.4	3.6	3.0	6
Acipenser Sturio .....	0	1.2	6.5	9.7
	3.1	7.5	7.5	17
Gadus Morrhua .....	0	0.6	15.6	24.5
	13.2	4.9	4.9	12
Squalus Acanthias .....	0	2.5	12.2	15.4

The distances are measured from the apex of the cornea.

The radii of curvature are in old-faced figures. Thus in the last the retina is 15.4 millims. from the front of the cornea, and its radius of curvature 12 millims.



LIX. *Remarks on the Dynamical Theory of Electricity.*

By C. BROOKE, M.A., F.R.S.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

Fitzroy Square, W.  
Nov. 10, 1866.

SINCE I sent to you, through Professor Tyndall, a short notice of a fact in thermo-electricity, I have had under revision my chapter on organic electricity, and have been forcibly impressed by the harmony existing between obvious deductions from the dynamical theory and some recently observed physiological results.

The physiological effects of acting causes incidental to the transmission of a continuous voltaic current through a musculo-motor nerve are of a complex character; they are universally acknowledged to be manifested *only* at the moments of closing and opening the circuit, but are modified by the influence of the current, during its prolonged continuous passage, on the portion of nerve-tissue included in the circuit.

In order to interpret correctly all the observed physiological effects, it becomes necessary to consider carefully the dynamical consequences of the passage of a continuous succession of electric waves, here assumed to constitute a voltaic current; and it will appear that the physiological results are remarkably in accordance with the dynamical theory of electricity. The passage of a voltaic current, then, must comprise three distinct phases: first, the momentary passage of the molecules of the conductor from a state of rest to a state of motion; secondly, the indefinite continuance of molecular motion; and thirdly, the return of the moving molecules to a state of rest.

The first phase will be accompanied by a rush, or sudden impulse of increased potential in the direction of the current, because there must be a condensation or accumulation of motion, in consequence of the inertia of the molecules *at rest* opposing the transmission of the wave: this may be termed the *initial* current. During the second phase there will be (supposing the potential of the current to remain constant for the time) continuous and uniform wave-motion. During the third phase, the excitation of motion ceasing, the *vis viva* of the moving particles will accumulate motion towards the termination of the conductor, whence a reflex motion may be expected to be propagated (as in the case of a wave travelling from the hand along a stretched cord, which reaching the fixed end, is reflected back again), giving rise to a momentary *terminal* current, inferior in intensity, and opposite in direction to the *initial* current.

These initial and terminal currents (or impulses, as they might  
*Phil. Mag. S. 4. Vol. 32. No. 218. Dec. 1866.* 2 F

more appropriately be termed) have long since been recognized as the *extra-currents* of Faraday; but their relative direction and intensity have been assumed to coincide with those of the induced secondary currents, and therefore to be the reverse of what dynamical considerations have suggested; it has, however, been demonstrated by an experiment of M. Chauveau, that the dynamical view is the correct one. It has been proved by numerous experiments that physiological effects are produced, and produced *only*, by a sudden efflux of electricity *from* a nerve or muscle *into* a negative electrode, whether the active agent be a discharge of Franklinic electricity, or either the induced or the extra currents, already mentioned. Starting from this as an admitted fact, the experiments of M. Chauveau appeal to the most sensitive of all tests of the direction of an electric impulse (using that term as synonymous with "shock" or "momentary current")—a living nerve. He places the electrodes of an electromotor over the opposite facial nerves of a horse, and, having duly adjusted the strength of the current, he finds that, on closing the circuit that side of the face only is convulsed (by the *initial extra-current*) the nerve of which lies under the *negative* electrode, and on opening the circuit the contrary side is *less strongly* convulsed (by the *terminal extra-current*), the nerve of which lies under the *positive* electrode. M. Chauveau also found that with a still further reduced current, convulsion occurred in relation with the negative electrode only, the contrary or terminal extra-current being then too feeble to affect the nerve. And if several horses were similarly included in one circuit, the same results were observed in each of them.

The same fact has been observed by M. Claude Bernard\* in a prepared frog's limb in which the vitality of the nerve is unimpaired: with a sufficiently reduced current convulsion occurs on closing the circuit, and only then, whether the current be direct or inverse, because the terminal extra-current is then inoperative.

It may here be remarked that the well-known relative direction and intensity of the initial and terminal secondary or induced currents in a secondary coil are the necessary dynamical consequences of the above assumed conditions of the extra-currents. The initial extra-current will excite a similar impulsive motion in the secondary coil, just as one stretched chord will excite another capable of vibrating in unison with it (for electro-dynamic induction is probably quite analogous to the reciprocation of sound); and the recoil of this impulse (the *initial induced current*) will be weakened in opposing the *continuous*

\* *Leçons sur la Physiologie et la Pathologie du Système Nerveux*, Paris, 1858, vol. i. p. 163.

motion induced by the *continuous* primary current. Again, the recoil of the impulse induced in the secondary coil by the terminal extra-current in the primary (the *terminal induced current*), will likewise be in a direction contrary to that of the inducing impulse, but its potential will remain undiminished, as it is unopposed by any continuous induction; and it will therefore possess greater force than the initial induced current.

But it may be asked by those who find a difficulty in dispossessing their minds of long-established and time-honoured notions, Is not all this about "inertia" and "vis viva" and "impulses" sheer hypothesis? Not so: the writer has long since observed and recorded a precisely similar phenomenon (apparently an exact analogue of the initial extra-current) in an unquestioned case of wave-motion—an experiment on the interference of sound-waves, due in common with so many others to the genius of Prof. Wheatstone. Let the handle of a vibrating tuning-fork, held obliquely, rest on the surface of a table: as long as it remains at rest, a loud resonance of the table is audible; but if the tuning-fork be moved parallel to itself along the surface of the table in any direction, the resonance of the table immediately ceases, from the perpetual interference of the vibrations in successive parallel planes with each other. The instant the tuning-fork stops, the resonance bursts out again in a very striking manner. If the tuning-fork be held vertically, the planes of vibration coincide, and the resonance is not interrupted by moving it. It can scarcely be doubted that the impulsive recommencement of the resonance, after its interruption by interference, is entirely due to the dynamical cause here assigned to the initial extra-current.

M. Chauveau (no doubt correctly) ascribes the physiological effect of an electric impulse to the dynamical molecular disturbance which it produces.

It will naturally be asked if electricity be only wave-motion, what is the nature of that motion, and in what respects does it differ from the wave-motion of light and heat? It is evident that the existence of two opposite electrical states must involve some kind of polarity or directionality in the motion, not required to explain the phenomena of light and heat. The probable dependence of magnetism on the circulation of electricity round the molecules of the magnet would seem to suggest the idea of circular waves; and if these be supposed analogous to the waves of circularly polarized light, the phenomena of electric polarity may be readily explained. Moreover the state of mutual inductive constraint of the electricity of two opposed and oppositely electrified surfaces may be roughly symbolized by the condition of two spiral springs, mutually compressing each other against an intervening obstacle.

In the hope that these remarks may induce some of your readers to direct their thoughts to the elucidation of an important point in physics,

I remain,

Yours faithfully,

CHARLES BROOKE.

LX. *Note on a Memoria Technica for Delambre's, commonly called Gauss's Theorems.* By Professor SYLVESTER, F.R.S.\*

THE most subtle reagents employed in spherical analysis and transformation are the following four admirable formulæ, "commonly ascribed to Gauss, but in reality due to Delambre"†:—

$$\cos \frac{c}{2} \cos \frac{A+B}{2} = \sin \frac{C}{2} \cos \frac{a+b}{2},$$

$$\cos \frac{c}{2} \sin \frac{A+B}{2} = \cos \frac{C}{2} \cos \frac{a-b}{2},$$

$$\sin \frac{c}{2} \cos \frac{A-B}{2} = \sin \frac{C}{2} \frac{\sin (a+b)}{2},$$

$$\sin \frac{c}{2} \sin \frac{A-B}{2} = \cos \frac{C}{2} \frac{\sin (a-b)}{2}.$$

Four out of the six binary combinations of these four equations give by simple division Napier's *Analogies*, a term which seems almost equally appropriate to designate Delambre's formulæ. It need hardly be remarked that whilst Napier's analogies may be immediately deduced from Delambre's formulæ, the converse is not true.

If we call the products on the left-hand side of the equation P, Q, R, S, and their polar reciprocals P', Q', R', S', it is worthy of notice that the formulæ become

$$P = -P', \quad Q = R', \quad R = Q', \quad S = -S'.$$

The formulæ may be expressed collectively by the easily remembered disjunctive elective equation

$$\frac{\cos c}{\sin 2} \frac{\cos A+B}{\sin 2} = \frac{\cos C}{\sin 2} \frac{\cos a+b}{\sin 2}.$$

\* Communicated by the Author.

† Todhunter's 'Spherical Trigonometry,' p. 27. See also Davies's edition of Hutton's Course, vol. ii. p. 37.



The number of products on each side of the equation, if all the combinations of trigonometric affection and algebraical sign are exhausted, is  $2^3$  or eight. Out of each 8, 4 only are to be preserved and colligated each with each. Thus the number of systems capable of formation is

$$\left( \frac{8 \cdot 7 \cdot 6 \cdot 5}{1 \cdot 2 \cdot 3 \cdot 4} \right)^2 (1 \cdot 2 \cdot 3 \cdot 4) = 24 \times 70^2 = 117600,$$

of which one only is valid. This accounts *à priori* for the difficulty of recollecting these formulæ, a difficulty often complained of and still oftener felt, and which is one reason of their being comparatively little used by junior students. Two observations easily retained in the memory will serve, I think, in a great degree to remove this difficulty.

*Rule 1.* On opposite sides of any one equation the trigonometric affections of the angles are contrary, and those of the sides similar.

*Rule 2.* The trigonometric affection of the uniliteral factor of each product governs the algebraic sign of the biliteral factor, in the following manner:—

Comparing products which lie on the *same* side of the equations, *like and unlike* affections go with like and unlike signs; comparing those which lie on *opposite* sides of the equations, *unlike and like* affections go with *like and unlike* signs.

These two rules are not quite sufficient in themselves; for they would be satisfied not only by the four true equations, but also by the four following false ones:—

$$\cos \frac{c}{2} \cdot \cos \frac{A-B}{2} = \sin \frac{C}{2} \cos \frac{a-b}{2},$$

$$\cos \frac{c}{2} \cdot \sin \frac{A-B}{2} = \cos \frac{C}{2} \cdot \cos \frac{a+b}{2},$$

$$\sin \frac{c}{2} \cdot \cos \frac{A+B}{2} = \sin \frac{C}{2} \cdot \sin \frac{(a-b)}{2},$$

$$\sin \frac{c}{2} \sin \frac{A+B}{2} = \cos \frac{C}{2} \sin \frac{(a+b)}{2}.$$

To make the system of rules complete so as to exclude *à priori* the construction of the four false deductions, it is necessary and sufficient to bear in mind that, on the left-hand side of the equation, the *cosine*-affection of the uniliteral term is associated with the *plus* sign in the biliteral one\*.

\* Rule 2, with the addition to it, may be easily retained in the memory by

But even without this check the false equations may be put to the question and made severally to disclose their character as such by applying any one of them to the limiting case of a triangle on a sphere continuing of *finite radius*, but in which the angles become respectively  $180^\circ$ ,  $0$ ,  $0$ , and consequently the side opposite the first equal or capable of being equal to the sum of the other two. Thus writing in the first and third of the last written formulæ  $C=180^\circ$ ,  $B=0$ ,  $A=0$ , we ought to be able to derive  $c=a+b$ , but find instead  $a=b \pm c$  in the first, and  $a=b+c$  in the third. And similarly in the second and fourth, writing  $A=180^\circ$ ,  $B=0$ ,  $C=0$ , we ought to be able to derive  $a=b+c$ , but find instead  $a=-b \pm c$  in the second, and  $a=-b+c$ , or  $a+b+c=360^\circ$  in the fourth. We might easily deduce other detective criteria from the reciprocal limiting case of a spherical triangle in which one side is zero and the two others each  $180^\circ$ , in which case the angle opposite the first augmented by  $180^\circ$  will equal the sum of the other two. Furthermore, using accents, as before, to denote polar reciprocation, the false system takes the form

$$P-P'=0, \quad Q+R'=0, \quad R+Q'=0, \quad S-S'=0,$$

in lieu of the true form,

$$P+P'=0, \quad Q-R'=0, \quad R-Q'=0, \quad S+S'=0.$$

A direct geometrical proof of these potent formulæ appears to be a *desideratum*.

K House, Woolwich Common,  
November 9, 1866.

aid of the scheme below written,

		left.	right.
cos	sin	+	-
		-	+

but, as subsequently shown in the text, the bordering of the square may be affixed at random, *i. e.* the words *left* and *right* or *cos* and *sin* may be interchanged without leading to any error but of a kind susceptible of immediate detection and remedy.

LXI. *On the Sources of the Fat of the Animal Body.* By J. B. LAWES, F.R.S., F.C.S., and J. H. GILBERT, Ph.D., F.R.S., F.C.S.\*

IN 1842, Baron Liebig† maintained that the fat of Herbivora must be derived in great part from the carbo-hydrates of their food, but considered that it might also be produced from nitrogenous compounds. MM. Dumas and Boussingault ‡ at first called in question this view; but subsequently the experiments of Dumas and Milne-Edwards§ with bees, of Persoz|| with geese, of Boussingault¶ with pigs and ducks, and of ourselves with pigs\*\*, were held to be quite confirmatory of Liebig's view, at any rate so far as the formation of fat in the animal body from carbo-hydrates was concerned.

In 1864, however, at the Bath Meeting of the British Association for the Advancement of Science, Dr. Hayden, of Dublin, read a paper before the Physiological Section, in which, basing his conclusions upon certain physiological considerations of a purely qualitative kind, he argued that fat was not producible in the body from sugar and allied substances, but that both eventually served for the production of carbonic acid and water; and sugar being the most readily oxidized, so saved the combustion, and favoured the storing of fat.

Again, in August 1865, at a Meeting of the Congress of Agricultural Chemists, held in Munich (at which one of the authors was present), Professor Voit††, from the results of experiments with dogs fed on flesh, maintained that fat must have been produced from the nitrogenous constituents of the food, and that these were probably the chief if not the only source of the fat, even of Herbivora. In favour of the probability of this view, Professor Voit refers to the formation of adipocere from nitrogenous substance; but he mainly relies upon the fact that, in experiments by Pettenkofer and himself in which large quantities of flesh were given to a dog, the whole of the nitrogen reappeared in the form of urea and in the fæces, whilst only a portion of the carbon was recovered in the urine, fæces, and the products of respiration and perspiration, from which it was concluded that some had been retained in the body, and had con-

\* Communicated by the Authors.

† Organic Chemistry of Physiology and Pathology, p. 81 *et seq.*

‡ Balance of Organic Nature, 1844, p. 116 *et seq.*

§ *Comptes Rendus de l'Académie des Sciences*, vol. xvii. p. 731.

|| *Ann. de Chim. et de Phys.* vol. xiv. p. 408 *et seq.*

¶ *Ann. de Chim. et de Phys.* vol. xiv. p. 419 *et seq.*; xviii. p. 444 *et seq.*

\*\* "On the Composition of Foods in relation to Respiration and the Feeding of Animals," Report of the British Association for the Advancement of Science for 1852.

†† *Versuchs-Stationen Organ.* vol. viii. No. 1, 1866, p. 23.

tributed to the formation of fat. That animals nevertheless do not become fat when fed upon very highly nitrogenous food, Voit considers sufficiently explained by the greater number of blood-corpuscles, the result of such diet, and the greatly increased activity of oxidation of nitrogenous substance under such conditions; whilst, on the other hand, the accumulation of fat when fat and carbo-hydrates are supplemented to a liberal nitrogenous diet he considers to be connected with the much less active oxidation of the nitrogenous substance and fatty matter that then takes place, rather than attributable to the direct production of fat from the carbo-hydrates.

In the discussion which followed the reading of Professor Voit's paper, Baron Liebig forcibly called in question Professor Voit's conclusions, maintaining not only that it was inadmissible to form conclusions on such a point in regard to Herbivora from the results of experiments made with Carnivora, but also that direct quantitative results obtained with herbivorous animals had afforded apparently conclusive evidence in favour of the opposite view.

Since the Munich Meeting, Hermann von Liebig, son of Baron Liebig, has written a paper on the subject\*, in which, admitting the probability that fat may be formed from nitrogenous substance, he nevertheless concludes that this is neither its only, nor even its chief source, in the ordinary feeding of Herbivora.

After referring to the leanness of the South Russian shepherds, who consume very large quantities of dried meat, and to the rotundity of the peasantry, especially the women, in districts where bread and fruits constitute the chief articles of food, H. von Liebig proceeds to illustrate the formation of fat from non-nitrogenous constituents of food by our domestic Herbivora, by the calculation of the results of numerous experiments made with cows in 1857, by Knop, Arendt, and Behr, in which the details as to food, live-weight, and quantity and composition of milk, were accurately recorded. According to the mode of calculation adopted, it appeared that, after deducting from the amount of nitrogenous substance taken in the food that estimated to be required by the system for other purposes, there was generally little or none remaining for the production of fat. In his calculations, however, H. von Liebig, besides taking into account the probable amount of nitrogenous substance stored up in increase with gain of weight, or set at liberty when there was loss of weight, as the case might be, deducted from the amount of nitrogenous substance given in the food, not only that required for the production of the caseine of the milk, but also

\* *Versuchs-Stationen Organ*, vol. viii. No. 3, 1866.



the whole of that estimated to be required for the mere sustenance of the animal (according to its weight) independently of gain or loss, or milk produced.

It is obvious, however, as pointed out by Voit, and as afterwards admitted by H. von Liebig, that if nitrogenous substance may break up into urea and fat (with other products), the amount estimated to be required for the mere sustenance of the body should not be considered inadmissible for the formation of fat as one of its products, and therefore should not be deducted (with that appropriated for the production of increase and of the caseine of the milk) from the amount supplied in the food in estimating whether or not it provided sufficient for the formation of the fat known or calculated to be produced.

H. von Liebig states that he selected experiments with cows as the basis of his illustrations, considering that, when in a normal state, the change in the solid substance of the body of the animal was comparatively small, if not indeed immaterial, and that the fixed products of the food, beyond what might be required for the mere maintenance of the body, were accumulated and easily estimated in the milk collected; whilst he considered, on the other hand, that the point in question could not be settled by reference to results relating to fattening animals, without the aid of an apparatus for the determination of the products of respiration and perspiration. We believe, however, that with a proper selection of fattening animals it may be satisfactorily illustrated without the aid of any such apparatus; and it is the object of this paper briefly to discuss the question of the sources of the fat of the animal body by reference to the results of experiments with such animals.

As already intimated, the objections of Dr. Hayden to the supposition that fat is formed from the carbo-hydrates of the food, were based upon physiological considerations of a qualitative, but not at all of a quantitative kind. Voit's argument was, on the other hand, founded upon strictly quantitative results, obtained, however, under conditions as to choice of animal and of food, in which the formation of fat, if it took place at all, must of necessity be attributed to the nitrogenous constituents consumed. H. von Liebig also relied upon quantitative results as the basis of his illustrations; but those selected, when properly considered, afforded, to say the most, only negative evidence on the point.

The question arises—What description of animal is the most likely to yield the most direct and conclusive evidence as to the source of the fat stored up in its body? Obviously the one which is fed more especially with a view to the production of fat, which consumes in its most appropriate fattening food a relatively large proportion of carbo-hydrates, and which yields a

large proportion of fat, both in relation to the weight of animal within a given time, and to the amount of food consumed. The following Table (I.), which summarizes the results of a great many direct experiments of our own\*, will show that of the ox, the sheep, and the pig—the most important of the animals fed and slaughtered as human food—the last pre-eminently supplies the required conditions.

TABLE I.—Comparative fattening-qualities of different animals.

	Oxen.	Sheep.	Pigs.
Relation of parts in 100 live-weight.			
Average of .....	16	249	59
Stomach and contents .....	11·6	7·5	1·3
Intestines and contents .....	2·7	3·6	6·2
Heart, aorta, lungs, windpipe, liver, gall-bladder and contents, pancreas, spleen, and blood. ....}	14·3	11·1	7·5
	7·0	7·3	6·6
Per 100 live-weight.			
Dry substance consumed in food per week.....	12·5	16·0	27·0
Increase yielded per week .....	1·13	1·76	6·43
Per 100 dry substance of food.			
Total dry substance in increase .....	6·2	8·0	17·6
Fat in increase .....	5·2	7·0	15·7
Total dry substance in urine and fæces .....	36·5	31·9	16·7
Average fat per cent.			
In lean condition .....	16·0	18·0	22·0
In fat condition.....	30·0	33·0	44·0
In increase whilst fattening.....	60·0	65·0	70·0

Looking first to the comparative structure of the animals, so far as it may be considered characteristic or indicative of the description of the food, it is seen that, of stomach and contents, the ruminant ox has a much larger proportion than the ruminant sheep, and the ruminant sheep in its turn much more than the non-ruminating pig. Consistently with these facts, we find that the ox consumes in its food a much larger proportion of

\* For the data upon which most of the average results given in the Table are founded, see "Experimental Inquiry into the Composition of some of the Animals fed and slaughtered as Human Food," Phil. Trans. Part II. 1859. In the estimates given "per 100 live-weight" and "per 100 dry substance of food," it is assumed that the oxen and sheep are liberally fed on oil-cake, clover-chaff, and roots, and the pigs on barley-meal alone; with different foods the results will, of course, be different.

only slowly digestible, or indigestible, cellulose than the sheep, and the sheep again very much more than the pig. The usual food of oxen and sheep, consisting as it does in large proportion of unripened or imperfectly ripened vegetable matter, is, in fact, essentially crude, containing not only a considerable amount of defectively elaborated and probably unassimilable nitrogenous substance, but also a large proportion of comparatively indigestible non-nitrogenous matter. Accordingly complexity and great capacity of stomach, and slow progress of the food through the organ, are characteristics of the structure and digestive process of the animals.

Of intestines and contents, on the other hand, the ox has a less proportion than the sheep, and the sheep considerably less than the pig.

In fact, the relatively very small proportion of stomach and contents, and relatively very large proportion of intestines and contents in the pig are very striking. But when we consider that his most appropriate fattening food consists of ripened seeds and highly starchy roots, containing little indigestible woody fibre, and their non-nitrogenous constituents almost wholly in the form of starch, the primary change of which is known to take place almost throughout the length of the intestinal canal, the reason of the relatively small proportion of stomach, and large proportion of intestines, seems to be at once apparent.

Passing from a consideration of the receptacles and, so to speak, first laboratories of the food, we will only remark, in reference to the remaining results given in the upper portion of the Table, that, of what may be called the further elaborating organs of the body, and their fluids—the heart, liver, lungs, blood, &c.—the proportion, taken in the aggregate, is strikingly similar in the three descriptions of animal.

The second division of the Table shows that, notwithstanding its much larger proportion of stomach and contents, the ox consumes, for a given live-weight within a given time, only about three-fourths as much dry substance of food as the sheep, and less than half as much as the pig with its very small proportion of stomach and contents. The ox gives, too, in proportion to a given live-weight within a given time, much less increase than the sheep, and only from one-fifth to one-sixth as much as the pig.

Reckoned in proportion to a given amount of dry substance of food consumed, the ox gives less both of total dry substance in increase, and of fat in increase, than the sheep, and only about one-third as much of either as the pig, whilst the ox voids of dry substance in fæces and urine the largest proportion, the sheep somewhat less, and the pig little more than half as much as the sheep, and less than half as much as the ox.

Lastly, the proportion of fat, whether reckoned in relation to the total weight of the body, or to the weight of the increase whilst fattening, is greater in the sheep than in the ox, and greater still in the pig.

Whilst referring to the connexion between the weight and capacity of the stomach and the character of the food, it will not be without interest to call attention to the gradation in the proportion from the ox to the sheep, from the sheep to the pig, and from the pig to man. Below is given the approximate average proportion of stomach, by weight, in 100 live-weight of each.

Oxen.	Sheep.	Pigs.	Man.
3.19	2.44	0.88	0.38

Without assuming that relative weight represents with numerical exactitude relative capacity or size, we nevertheless cannot doubt that these figures have a very obvious significance. Thus, the ox consumes the largest proportion of difficultly digestible or indigestible woody-fibre, the sheep less, the pig scarcely any, but a much larger proportion of comparatively easily digestible starch, whilst man, within certain limits, the better he is fed the less does the non-nitrogenous portion of his food consist of starch, and the more of the much more highly concentrated alimentary substance fat, produced for him from much less concentrated vegetable food-materials by the animals which he feeds for his own consumption.

From the facts which have been briefly stated, it will be obvious that, of the most important animals which we feed for human food, the pig offers many advantages as a subject for the consideration of the source in the food of the fat which he yields. Thus, for a given live-weight he comprises a comparatively small proportion of alimentary organs and contents, and he consumes a large proportion of food, and yields a large proportion both of total increase and of fat, within a given time; his food is, as such, of a high character, yielding, compared with that of oxen or sheep, for a given weight of it much more total increase, much more fat, and much less excreted and necessarily effete matter; whilst his proportion of fat is the greatest, both in a given live-weight and in his increase whilst fattening. It results that changes in his live-weight are in a much less degree likely to be influenced by variation in the amount of the contents of the stomach and intestines, and are therefore much more direct indications of real increase of the substance of the body, and hence that there is much less probable range of error in calculating the amount and composition of the increase in live-weight in relation to the amount and composition of the food consumed.



In fact, from the very opposite characters of the ruminant in these respects, it is very much less appropriate for the purpose of estimating the sources in its food of the fat of its body. It is true that there is the advantage with the cow, that that important product of the food—the milk—is collected externally to the body, and hence its amount and composition can be easily determined; but the changes of weight of the animal itself, though comparatively small, are due to a greater variety of circumstances, and can, therefore, with less of certainty be properly interpreted than even in the case of either the ox or the sheep. Indeed, when experiments are conducted with cows or oxen, or even with sheep, for periods of a few weeks only, the variation in live-weight may in very great proportion be due to variation in the contents of the alimentary organs merely.

The selection and calculation of results brought to view in Table II. will show that, when experiments are conducted with pigs fed on good fattening food for periods of not less than eight or ten weeks, the amounts both of total increase and of fat stored up are so great in proportion both to the original weight of the animal and to the food consumed, that the data so obtained may be safely relied upon as a means of estimating, with sufficient accuracy for the purposes of the present discussion, from what constituent or constituents of the food the fat of the animals has been derived.

*Experiment 1.*—In this experiment two pigs of the same litter, of equal weight, and, as far as could be judged, of similar character, were selected. One was killed at once, and the amount of total dry or solid matter, nitrogenous substance, fat, and mineral matter, in its body, determined. The other was then fed for a period of ten weeks on a good mixed food, containing, however, a more than usually high proportion of nitrogenous substance. It was then weighed and killed, and its composition was determined as in the case of the other animal. The results so obtained supplied an important portion of the data requisite for the calculation of the composition of the increase in the other cases\*. The food consisted of a mixture of bean-meal, lentil-meal, and bran, each one part, and barley-meal three parts, given *ad libitum*.

\* For further details relating to this and the other experiments, we must refer to our former papers, as follow:—"On the Composition of Foods in relation to Respiration and the Feeding of Animals," Report of the British Association for the Advancement of Science for 1852. "Agricultural Chemistry: Pig Feeding," Journ. Roy. Ag. Soc. Eng. vol. xiv. part 2, 1853. "On the Equivalency of Starch and Sugar in Food," Report of the British Association for 1854. "Experimental Inquiry into the Composition of some of the Animals Fed and Slaughtered as Human Food," Phil. Trans. part 2, 1859.



*Experiments 2 & 3.*—In both these experiments the proportion of nitrogenous substance in the food was very large; the relation of non-nitrogenous to one of nitrogenous substance being in Exp. 2 little more than half, and in Exp. 3 little more than one-third as much as is usual in the recognized good fattening food of the animal. In Exp. 2 the food consisted of bran, bean and lentil-meal, and Indian-meal, each given separately, and *ad libitum*; and in Exp. 3 of an equal mixture of bean and lentil-meal only, given *ad libitum*.

*Experiments 4 & 5.*—In Exp. 4 the food consisted of Indian meal only, and in Exp. 5 of barley-meal only, in each case given *ad libitum*. Barley-meal is undoubtedly the most approved staple fattening food of the pig; and the result was, that in both these experiments the proportion of non-nitrogenous to nitrogenous substance in the food was very nearly, though rather higher than, the average in that which is recognized as the most appropriate fattening food of the animal.

*Experiments 6, 7, 8, & 9.*—The peculiarity of this series was, that the food contained less ready-formed fat than was the case in either of the other experiments, and that a large proportion of the non-nitrogenous substance supplied was in the form of either pure starch, pure sugar, or both. In Exps. 6, 7 & 8, a fixed quantity of lentil-meal and bran (averaging nearly  $3\frac{1}{4}$  lbs. lentil-meal and about 9 ounces bran) was given per head per day, and, in addition, in Exp. 6 sugar, in Exp. 7 starch, and in Exp. 8 sugar and starch, each separately, *ad libitum*. In Exp. 9 lentil-meal, bran, sugar, and starch were each given separately, *ad libitum*.

The figures given in the Table show that the increase in weight was in no case less than 50, and in several nearly, and in one more than 100 per cent., upon the original weight of the animals, the amounts ranging from 51·3 to 68·9 per cent. when the experiment extended over eight, and from 85·4 to 106·8 per cent. when it extended over ten weeks.

The determined or estimated amount of fat stored up in the increase was also in all cases very large, amounting to 63 per cent. of the total increase in Exp. 1, in which it was experimentally determined, and calculated to be even more than this in several of the other cases. The tendency to error in the calculations would, however, be to give the proportion too low in Exps. 6, 7, 8 & 9, which were conducted over a period of ten weeks, and in which the proportion of increase upon the original weight was very high, and to give it too high in Exps. 2, 3, 4 & 5, conducted only over eight weeks, but more especially in Exps. 2 & 4, in which the proportion of increase upon the original weight was comparatively small. The rang

of the probable error of calculation here indicated is, however, not such as in any degree to throw doubt upon the validity of any conclusions which will be drawn from the indications of the figures as they stand.

It is seen that, of the determined or estimated total fat stored up in the increase, the proportion which could possibly have been derived from the ready-formed fat of the food, even supposing the whole of that supplied had been assimilated, was so small as to leave no doubt whatever that a very large proportion of the stored-up fat must have been produced from other constituents than the ready-formed fatty matter of the food. According to the figures given in the Table, the proportion of fat which must have been so produced, ranged from about two-thirds to about eight-ninths of the total amount stored up.

Assuming it, then, to be established beyond doubt that there was a very large formation of fat within the body from other constituents than the fatty matter of the food, the questions arise, whether this large amount of produced fat could possibly have been derived from the nitrogenous constituents of the food? or whether it must of necessity have had its source, in greater or less proportion, in the carbo-hydrates at the same time supplied? The results adduced afford conclusive evidence on this point also.

The figures show that, after deducting from the total amount of nitrogenous substance consumed for the production of 100 lbs. of increase in live-weight the small amount estimated to be stored up in the increase, there remains a very large proportion available, it may be, for the production of fat with other products.

If we next compare the amount of carbon in the estimated *produced* fat with the amount contained in the nitrogenous substance of the food not stored up as increase, *minus* that contained in the urea which would be one of the final products of the breaking up of this nitrogenous substance (or its equivalent given off), the result shows in some cases an excess, and in others a deficiency, of carbon possibly available from the nitrogenous constituents of the food, compared with that required for the formation of the fat estimated to be derived from other constituents than the ready-formed fat in the food.

Reckoned to the standard of 100 carbon in the estimated produced fat, it is seen, as shown in the two bottom lines of the Table, that in Exps. 1, 2 & 3, in which the proportion of non-nitrogenous to nitrogenous substance in the food was (especially in Exp. 3) considerably less than in such food as experience has shown to be the most appropriate in the fattening of the pig—that is to say, in which the nitrogenous sub-



stance was in considerable excess over the amount and proportion usually supplied—there was, according to the calculation, more than sufficient carbon possibly available from the nitrogenous substance of the food for the formation of the fat estimated to be produced.

In Exps. 4 & 5, however, in which the relation of the non-nitrogenous to the nitrogenous substance in the food was much more nearly that in the usual food of the well-fed fattening pig, it is reckoned that there was about 40 per cent. of the carbon of the produced fat which could not possibly have been supplied from the nitrogenous constituents of the food.

In the other experiments (Nos. 6, 7, 8 & 9), in which again the proportion of the non-nitrogenous to the nitrogenous constituents of the food was lower than usual (though not so much so as in Exps. 1, 2 & 3)—in which, in fact, the nitrogenous constituents were in excess—there was still a considerable proportion of the carbon of the produced fat which the nitrogenous constituents of the food could not possibly have supplied.

It is hardly necessary to point out that, according to the mode of illustration we have adopted, the figures show not only the utmost proportion of the carbon of the stored-up fat which could possibly have had its source in the nitrogenous substance of the food, but even notably more than could possibly have been so derived. Thus, to say nothing of other considerations, it has been assumed for simplicity of illustration, and granted for the sake of argument, that the whole of the ready-formed fatty matter of the food contributed to the fat stored up, that the whole of the nitrogenous substance of the food not stored up as increase would be perfectly digested and become available for the purposes of the system, and that in the breaking up of the nitrogenous substance for the formation of fat no other carbon-compounds than fat and urea would be produced. It is obvious, however, that these assumptions are in part improbable, and in part quite inadmissible, and that the tendency of each of them is to show too large a proportion of the produced fat to have been possibly derived from the nitrogenous constituents of the food.

The amount of fat necessarily derived from other sources than the nitrogenous constituents of the food must therefore be greater than our mode of estimate can indicate; and it is obvious, from the figures given in the Table, that the less the excess of nitrogenous substance in the food, the greater was the proportion of produced fat which must necessarily have had its source in the carbo-hydrates of the food, and that, at any rate in those cases in which the proportion of non-nitrogenous to

nitrogenous constituents supplied was the more nearly that occurring in the admittedly most appropriate fattening food of the animal, the proportion of the fat which must necessarily have been derived from the carbo-hydrates was very large, even allowing all that was possible to have been produced from the nitrogenous substance of the food.

That, nevertheless, fat may be produced in the animal body at the expense of nitrogenous substance, in greater or less degree according to the character of the animal and of the food, not only chemical and physiological considerations, but direct experimental evidence would lead us to conclude. Indeed we have, in former papers already referred to, called attention to the fact that the results of our experiments with fattening animals, when carefully considered, afford evidence in favour of such a conclusion. To discuss the point satisfactorily on the present occasion, by the aid of figures, would, however, unduly extend the limits of our paper.

But, as indicating the bearing of the results referred to, it may be stated, in passing, that in numerous cases, otherwise comparable, but in which the amount and proportion of the nitrogenous constituents consumed varied very greatly, the results clearly showed that neither the amount of food consumed, nor the amount of increase in live-weight produced, bore any direct relation to the amount of nitrogenous substance supplied. On the other hand, both the amount of food consumed and the amount of increase produced bore a very close relation to the supply of digestible non-nitrogenous constituents, and even a closer relation still to the amount of total digestible dry organic substance (that is, nitrogenous and non-nitrogenous taken together) ; whilst, so far as could be judged from careful observation, the proportion of nitrogenous to non-nitrogenous substance (fat) in the increase did not vary in anything like a corresponding degree with the variation in the proportion of the nitrogenous and non-nitrogenous constituents in the food. The animals consuming excessive amounts of nitrogenous substance did, indeed, show a greater tendency to increase in frame and flesh ; but they nevertheless became fat. It would appear that the excess of nitrogenous substance had acted vicariously in defect of a greater supply of the non-nitrogenous constituents, contributing material not only to meet the respiratory exigencies of the animal, but also for the production of fat.

The main conclusions in regard to the sources of the fat of the animal body to which the evidence adduced has led, may be briefly stated as follows :—

1. That certainly a large proportion of the fat of the Herbi-

vora fattened for human food must be derived from other substances than fatty matter in the food.

2. That when fattening animals are fed upon their most appropriate food, much of their stored-up fat must be produced from the carbo-hydrates it supplies.

3. That nitrogenous substance may also serve as a source of fat, more especially when it is in excess and the supply of available non-nitrogenous constituents is relatively defective.

LXII. *On the Influence of Magnetization on the Length and the Resistance of Iron Bars.* By W. BEETZ\*.

WIEDEMANN† and Buff‡ have both expressed opinions as to the molecular actions which occasion a lengthening in an iron bar when it is magnetized. From these actions we may expect on the one part a lengthening, on the other part a shortening of the bar. For it may be supposed—

(1) On the theory of magnetic fluids, that a shortening of the bar occurs in consequence of the mutual attraction of molecules which have become magnetic.

(2) On Ampère's theory, that the parallel currents attract each other, whereby the bars are shortened.

(3) That the molecular magnets set with their long axis parallel to the axis of the bar, and thus produce a lengthening of the bar,—a view which De la Rive§ has expressed, and to which Tyndall|| and Buff adhere.

(4) That, by magnetizing, a mechanical pull is exerted on some parts of the bar, which lengthens it, as was observed by Wertheim¶.

(5) That the bar was previously twisted or bent, and that magnetization stretches it by removing this.

In fact, both a lengthening and a shortening action have been observed in the magnetization of iron bars: Joule\*\*, Wertheim, and Buff have undoubtedly shown a lengthening, and Tyndall†† has even demonstrated it by a lecture-experiment; Joule has further shown that, instead of a lengthening, there is a shortening if the bars or wires are under a strong strain.

From the supposed molecular actions, conclusions may be drawn

\* Translated from Poggendorff's *Annalen* for June 1866.

† *Lehrbuch des Galvanismus*, vol. ii. p. 457.

‡ Liebig's *Annalen*, Supplementary volume iii. p. 136.

§ *Ann. de Chim. et de Phys.* ser. 3. vol. xxvi. p. 158.

|| *Cosmos*, vol. xxiv. p. 719.

¶ Poggendorff's *Annalen*, vol. lxxvii. p. 43.

\*\* *Phil. Mag. S. 3.* vol. xxx. p. 76. †† *Cosmos*, vol. xxiv. p. 718.



in regard to the changes which the resistance of an iron wire experiences during magnetization. From the first two processes, which are in fact identical, the conclusion must be drawn that the resistance is diminished by magnetization; for the contact between the molecules in the direction of the length becomes closer, and the entire length diminishes; by the third process the contact is closer indeed, but the bar becomes longer and thinner; thus there may be either an increase or a decrease in the resistance, according as one or the other action predominates. The fourth action must necessarily increase the resistance; in the fifth there appears no reason why the resistance which it produces should be altered either in one direction or the other.

The experiments of Wartmann\*, Mousson†, and Edlund‡ have not shown any change in resistance during magnetization, while Thomson§ observed an increase of resistance in the direction of the magnetic axis, and a diminution in a direction at right angles thereto. In discussing these discordant results, Wiedemann|| has suggested that in many of Thomson's experiments it was possible that the attraction of the poles had exerted a purely mechanical pull on the iron between them, by which it would be extended in an axial, but drawn together in an equatorial direction; and I must confess that in reference to the other experiments of the same observer I had from the first a suspicion that the alteration in resistance is an entirely secondary phenomenon, produced by the alteration in the length of the bars. It is true that the increase in resistance which Thomson observed is so considerable that it cannot be directly explained on Ohm's law from that alteration in length, not even if we remember that such an alteration in length must be accompanied by a diminution of the section if the volume remains constant; and neither Joule nor Wertheim nor Buff has been able to show that there is any change in volume. Yet Mousson's experiments, in which wires were stretched by weights, showed such an unlooked-for increase in resistance, that its chief reason must be sought in the removal of the molecules from each other. Experiments which I have made on the alteration in length and in resistance have shown that my supposition was not correct.

The bars whose lengths were to be measured were fastened at one end in a horizontal position, and were supported in several places by easily moveable rollers. From the free end of the bar a string passed which was coiled round a vertical steel axis, then passed over a pulley, and was stretched by a weight. On the

\* *Arch. des Sc. Phys.* vol. xiii. p. 35.

† *Ibid.* vol. xxxi. p. 111.

‡ *Poggendorff's Annalen*, vol. xciii. p. 315.

§ *Phil. Trans.* 1856, p. 315.

|| *Lehrbuch des Galvanismus*, vol. ii. p. 466.



steel axis was a plane mirror, in which the image of a scale could be read off by means of a telescope and cross wires. The magnetizing spirals were those belonging to a large Kleiner's electro-magnet—two of 53 millims., two of 75 millims. diameter, and each 23 cubic centims. in length. In case no other fixing was required, they were so arranged that the two outside spirals (the narrow ones) were flush with the ends of the bar, while the two inner ones (the wider) were at equal distances from each other and from the outer ones. The scale was so divided that one division corresponded to 1.270 millim., while the distance of the scale from the steel axis was 3220 millims. Hence a displacement of one division of the scale corresponded to an angle of rotation of the mirror of  $40''\cdot71$ . The radius of the steel axis, calculated from the weight and specific gravity of the wire and from its length, =  $0\cdot14072$  millim.; so that a motion over one division corresponded to an increase in length of the bar of  $0\cdot00008698$  millim. The magnetizing current was each time arranged in such a manner that very nearly the maximum magnetizing effect was obtained. The numbers given below for the elongations are the means of at least six observations in each case, which always agreed very closely with each other.

From the length and width of my spirals, it might have been expected that small motions of the bars out of the axis of the spirals would have but little influence on the apparent change in length, which occurred in consequence of the tendency of the bar to go to the axis of the spiral. In order to settle this point I observed these changes, first when the bar was centred as completely as possible, then when all the spirals were placed obliquely, again when the bar almost touched their inner coils, and finally when it was again well centred. The bar was a cylinder 1242 millims. in length and 12 millims. in thickness.

The elongation was—

Bar well centred . . . . .	11.7 divisions
Spirals oblique . . . . .	11.6 „
Spirals almost touching the bar . . . . .	10.3 „
On repeatedly opening and closing the current . . . . .	9.1 „
	8.8 „
	8.5 „
	8.2 „
	7.0 „
Bar again centred . . . . .	11.6 „

Hence any appreciable influence of the measurements could only be due to a very considerable eccentricity, which could not arise from an accidental displacement. That the readings are less in

an extreme position could only be due to the circumstance that the bar could not move parallel to itself, but always made an increasing angle with the axis.

The measurements made with iron bars and with thick iron wires gave the following values, in which  $L$  indicates the length of the bar,  $d$  its thickness, both in millimetres, and  $\Delta$  its expansion when the maximum magnetization was attained:—

No.	L.	d.	Displacement.	$\frac{L}{\Delta}$
1	966	1.3	0.8	13880000
2	922	4	0.5	21200000
3	1250	6	6.5	2310000
4	1242	12	11.0	1230000
5	1175	28	6.4	2110000
6	1010	12	0.0	42440000
According to Joule .....				720000
" Buff .....				420000
" Wertheim .....				500000

In all these measurements the stretching was effected by a weight of 1 kilog. No. 6 was a four-edged steel bar, which indicates considerably smaller extensions than the iron bars. The

reason why in these also, the values  $\frac{L}{\Delta}$ , were greater than those

found by Joule, Wertheim, and Buff consists doubtless in the fact that my iron bars were not specially heated and slowly cooled. As the object of these experiments was only to test the applicability of my method, and not to determine the absolute values of the angles of rotation with greater accuracy than had been done previously, I have made no further measurements in this direction; but I tried, by various positions of the magnetizing spirals, to decide which of the above processes are most favourable for stretching. For this purpose the stretchings were observed when the four spirals were spread, as above, over the whole bar, when, two being stuck in each other, all four were placed in the middle, all four on the fixed end, and all four on the free end, each two on each end of the bar, and, lastly, two on the middle and two on one end. Besides this, the temporary magnetism of the bar was determined while the spirals occupied the above position. The bar was in an east-to-west direction, at a distance of 4 metres from the magnetometer. In the numbers given for the temporary magnetism, the displacements due to the spirals alone, and those due to remanent magnetism, have been already deducted. During the whole range of the experiments the current was kept at a constant strength.

	Position of the spirals.	Magnetism.	Extension.
<i>a</i>	4 in the middle .....	46.62	3.7
<i>b</i>	2 in the middle, 2 at the free end .....	41.09	5.8
<i>c</i>	4 at the free end .....	43.91	5.8
<i>d</i>	Distributed .....	42.30	4.6
<i>e</i>	2 in the middle, 2 at the fixed end .....	40.63	3.5
<i>f</i>	4 at the fixed end .....	36.81	0.9
<i>g</i>	Two at each end .....	30.81	3.3

These numbers show distinctly how considerable is the part which the mechanical pull exerts in the extension of the bars. In the position *c* the extension is much greater than in *a*, although the momentum of the bar is less. In *g* the extension is almost the same as in *a*, although the momentum is a third less. In *f* the extension is inconsiderable, although the momentum is greater than in *g*. Buff has also called attention to the cooperation of this mechanical pull.

If, then, it has not only been shown that magnetizing lengthens the bars, but also that that lengthening more especially comes into play which tends to remove the molecules apart, it seems as if the increase in resistance observed by Thomson might be very easily explained. But the experiments with stretched wires do not agree with this. For these, the arrangement formerly used was applied without any change. The wires were surrounded by a tube through which a current of water passed. I obtained the following changes in length with three different wires (the plus sign indicating an elongation, the minus sign a contraction):—

No.	Wire.	L.	<i>d</i> .	Tension.	Change in length.
		mm.	mm.	grms.	divisions.
7	Hard .....	1250	1.3	1000	— ?
	Annealed .....	.....	.....	1000	— 4.7
				20000	— 0.3
8	Hard .....	1250	0.28	1000	— 0.2
	Annealed .....	.....	.....	1000	— 0.9
9	Covered .....	1250	0.24	300	+ 1.0
				500	0
				1000	— 0.2
	Annealed .....	.....	.....	100	— 1.0
				300	— 0.9
				1000	— 0.8
				100	— 0.1
	Covering dissolved off in sulphuric acid. ....	.....	.....	300	0
				500	— 0.1
				1000	— 0.4

Wire No. 7, when magnetized, vibrated so strongly that a qualitative determination of the contraction was not possible. The annealed wire also vibrated strongly. The tension 20000 grms. was produced by a lever which was fastened at one end of the wire. The results obtained are easily accounted for if we assume that the stretching separated the molecules of the magnet, while the magnetization brought them together. If the tension is too great, the contraction is only produced with difficulty, and may not occur at all. The different contractions which wire 8 undergoes, in the hard and in the soft condition, cannot possibly be explained from the different ductility of the wire; it is rather to be supposed that the wire was bent, and that the stretching weight, 1000 grms., could straighten the soft but not the hard wire, that in this case a lengthening was opposed to the contraction. It may be supposed that this was also the case with the wire 9, where in the last case the covering was removed, not by heating, but by dipping in concentrated sulphuric acid. With a tension of 300 grms. the covered wire is still stretched (partly, no doubt, because the coating bears a good deal of the stretching weight), the uncovered but hard wire remains unchanged; the soft is even more strongly stretched than is necessary for its maximum contraction.

I obtained entirely similar results on placing the apparatus of observation in a vertical position. The iron wires were soldered to a quadrangular piece of brass which moved up and down in a brass sheath, and could be fastened by a screw. The magnetizing spirals were fastened on consoles in the wall. At the end of the wire was a second quadrangular piece which passed through a guide. To this piece of brass was attached the thread which was coiled about the axis of the mirror and supported the stretching weight. The distance of the scale from the mirror was 4207 millims.; so that a displacement on the scale amounting to one division corresponded to an increase in the length of the wire of 0.00006658 millim. This vertical arrangement of the apparatus enables the wire to be very accurately adjusted on the spiral axis; and moreover the guiding at the lower end is a guarantee against the action of the twisting of the wires. The screw at the top makes it easier to find the image of the scale in the mirror, and to fix its zero-point upon the cross wires. The displacements of the scale found were the following:—



No.	Wire.	L.	d.	Tension.	Alteration in length.
10	Annealed ...	mm. 2035	mm. 0.24	grms. 200	divisions. -0.2
				300	-0.4
				400	-1.8
				600	-2.8
				800	-3.3
				1000	-3.4
11	Covered .....	2035	0.36	100	-0.1
				200	-0.1
				400	-0.2
				600	-0.3
				1000	-1.0
	Annealed ...	.....	.....	100	-2.0
				200	-1.8
				800	-1.5
				1000	-1.4

The annealed wire 11 had already exceeded the maximum of contraction at a tension of 100 grms. It is possible that it still contained small bendings, which could only be removed by greater tensions; yet these bendings must always have occurred again with smaller tensions, for the order of succession of the experiments had no influence on the results. On the other hand, in the case of wire No. 10 it is very distinctly seen how the magnetization always effects greater contractions with increasing tension, as Joule found to be the case.

The experiments with stretched wires lead definitely to the conclusion that in magnetization there is an approximation of the molecules; and the supposition is obvious that there must be a *decrease* of resistance during this process. To examine this point, both the quadrangular pieces of brass through which the wire was stretched were provided with binding-screws, from which wires passed to a Siemens's resistance bridge. The bridge, as in former experiments\*, was connected with a small rheochord, by which, when the measuring-wires had the ratio 10 : 1, a resistance of 0.0005 could be estimated. Immediately after the alteration in the length of the wire had been measured, its resistance was determined; the magnetizing current was then closed, and the alteration of resistance observed. Such an alteration always occurred, and it was found that the resistance of the iron was always increased by magnetization. In each wire the increase of resistance remained the same within the limits of observation, whether the tension was small or large, which could be recognized from the fact that the scale was always displaced the same number of divisions. There were no influences which

\* Poggendorff's *Annalen*, vol. cxvii. p. 5.

could have caused an error with respect to the origin of these deflections: the magnetizing spirals were at a distance of 12 metres from the galvanometer; and, to ensure greater certainty, the measuring current in the bridge was first sent in one direction and then in the other, by which the deflections were made opposite in direction, but they continued equal in amount. An inversion of the magnetizing current, on the contrary, produced no effect. The resistances measured were as follows:—

No.	Wire.	Tension.	Resistance.	
			Unmagnetized	Magnetized.
10	Annealed ...	grms.		
		400	7·2960	7·2985
		600	2970	2995
		1000	2990*	3015
11	Covered .....	100	4·2795	4·2820
		200	2800	2825
		400	2820	2845
		600	2828	2855
		1000	2805	2830
	Annealed ...	0	4·4025	4·4050
		100	3830	3855
		600	3840	3865
		1000	4870	4895
		2000	4105	4130

The following experiments were made with greater lengths than the apparatus previously used permitted.

No. 12. An iron wire of 1·3 millim. diameter was bent backwards and forwards ten times, so as to form a bundle 270 millims. in length; the individual layers were carefully insulated by means of sheet gutta percha, and the bundle, surrounded by the cooling-tube, was placed in a magnetizing spiral 230 millims. in length.

No. 13. A bundle of covered wire 0·36 millim. thick was made, 270 millims. in length and in 100 layers.

No. 14. A bundle, 190 millims. in length and in 142 layers was made of the same kind of wire.

No. 15. A wire 0·24 millim. thick was stretched backwards and forwards between two wooden disks, so that it formed 32 layers each 1390 millims in length. One disk was suspended at its centre, and on the other a weight of 10 kilogrammes hung; so that

\* These three experiments were made in rapid succession. The increase in resistance with the tension quite corresponds to the statement which Mousson has made. The following series was made on different days, so that individual experiments are not always comparable, owing to small differences in temperature.

each individual wire was stretched on the average by a weight of 312 grms. These wires were surrounded by all four spirals. In these four series of experiments the following results were obtained:—

No.	L.	d.	Tension.	Resistance.	
				Unmagnetized	Magnetized.
12	2700	1.3	grms. 0	0.3417	greater
13	27000	0.36	0	59.527	59.563
14	26980	0.36	0	58.500	58.534
15	44480	0.24	312	160.870	160.920

In these and in the previous series, wires were used which in previous experiments shortened on being magnetized (10, 11, 15), such as lengthen (12, 13, 14), bundles whose ends were within (14), and those whose ends were outside the ends of the spirals (12, 13): under *all* circumstances an increase of resistance was observed; its magnitude  $z$  is seen from the following Table:—

No.	Resistance = $w$ .	$z$ .	$z : w$ .
10	7.2990	0.0025	1 : 2920
11	4.2805	0.0025	1 : 1710
12	0.3417	not measurable.	
13	59.527	0.036	1 : 1650
14	58.500	0.034	1 : 1670
15	160.870	0.050	1 : 3220

Wires 10 and 15 were taken from the same coil, as also were wires 11, 13, and 14. The increase in resistance for the first amounts on the average to 1 : 3070 (Thomson found 1 : 3000); for the second, 1 : 1680.

I think these experiments justify the conclusion that *magnetization in all cases increases the resistance of iron in the direction of the magnetic axis*. I think, further, that I can account for the process which brings about this increase. One consequence of magnetization must be an approximation of the molecules. If the molecular distances in all parts of an iron bar were the same, a necessary consequence of this approximation would be a decrease in resistance. But the molecular distances are not everywhere the same; the molecules are rather arranged in groups—in a line, for instance, thus:—

... ..

and

... ..

the distances between the *sets* or groups being a little greater in the latter than in the former line.

In magnetization, the nearest molecules will become still nearer; and as the entire groups of molecules cannot have an arbitrary free motion, in some places there will be greater breaks even when the entire wire is shortened, as in the following scheme:

... ..

The resistance must thereby be increased; but to what extent, depends on the nature of the iron. If the groups of molecules had free motion, the magnetization would necessarily induce a decrease in resistance. And in fact if a glass tube be filled with fresh iron filings and the two ends of a battery placed in the ends, scarcely any current passes through the filings. In an experiment of this kind the current of two Daniell's cells only deflected the mirror of my reflecting galvanometer about 45 divisions: when the tube was magnetized in a spiral, the deflection increased to 120; on shaking the tube, to 450; on interrupting the magnetizing current, it sank to 170; and by a second shaking, to 14.

The decrease of resistance in the direction at right angles to the magnetic axis still requires explanation. The experiments of Thomson are, indeed, such that a mere mechanical pull must necessarily be succeeded by such a decrease; but they prove nothing as to the specific action of magnetization. I folded a covered wire of 47500 millims. in length and 0.36 millim. thickness in 332 coils about a rectangular glass plate, and placed this in a magnetizing spiral. To prevent the excitation of a current of induction in the iron wire, 160 coils were passed in one, and 166 in the other direction about the glass plate. The wire interposed in the bridge offered the resistance 99.195: when the magnetizing current was closed, there was not the least motion in the mirror of the galvanometer, although the wire was now magnetized at right angles to its length. An alteration of 0.0055 in the resistance would have displaced the scale by a whole division; hence if for these small values the displacements are assumed to be proportional to the alterations in resistance, a decrease of resistance in the proportion of 1:3000 would have effected a displacement of six divisions. As a displacement of 0.1 division is very distinct, a decrease in the resistance in the ratio of 1:18000 could not have been overlooked; so that I think I can fairly draw the conclusion that *a decrease of resistance in a direction at right angles to the magnetic axis has not been demonstrated.*

Erlangen, March 1866.



LXIII. *Note on the Properties of the Test Operators which occur in the Calculus of Invariants, their Derivatives, Analogues, and Laws of Combination; with an incidental application to the development in a Maclaurinian series of any power of the Logarithm of an augmented Variable.* By PROFESSOR SYLVESTER, F.R.S.†

SUPPOSE  $\phi_1$  denotes any algebraical function of the two sets of elements,

$$\left(a, b, c, \dots, \frac{d}{du}, \frac{d}{dv}, \frac{d}{dc}, \dots\right).$$

Let  $\psi*$  in general signify the process of operating with  $\psi$  upon all that follows‡.

Suppose  $\phi_1 * \phi_1 = \phi_2$ , where the operating elements  $\frac{d}{du}, \frac{d}{dv}, \dots$  of course can only operate upon the operands  $a, b, c, \dots$  in the second  $\phi$ . In like manner, let

$$\phi_1 * \phi_1 * \phi_1 = \phi_1 * \phi_2 = \phi_3,$$

and in general

$$(\phi_1 *)^{n-1} \phi_1 = \phi_n.$$

It will follow from this that

$$\phi_1 * \phi_1 * = (\phi_1^2 + \phi_2) * ,$$

$$\phi_1 * \phi_1 * \phi_1 * = (\phi_1^3 + 2\phi_1\phi_2 + \phi_3) * \S ;$$

† Communicated by the Author.

‡ The symbol of an operator consists of two parts, the *corpus* or quantity, and the *asterisk* or sign of operation. Thus a simple extensor operator has one of the extensors for its corpus; a compound extensor operator has any algebraical function of any number of extensors for its corpus. The operator which represents the combined effect of two or more operators following each other in any specified order may be termed their resultant; the theorems in the text amount to saying that the resultant of any number of simple or compound extensor operators is independent of the order in which its components occur, and is equivalent to some third compound extensor operator. One great problem to be solved is to determine the corpus of a resultant in terms of the corpora of its two components. This is done in the text for the simple case where each component corpus is a simple power of one of the extensors. To attain clearness of conception, the first condition is *language*, the second *language*, the third *language*—Protean speech—the child and parent of thought.

§ So more generally if  $\phi, \psi$  be any two functions of  $a, b, c, \dots, \frac{d}{du}, \frac{d}{dv}, \frac{d}{dc}, \dots$  we have

$$\phi * \psi * = (\phi \psi) * + [\phi * \psi] * ,$$

and in the general case there will be found no great difficulty in obtaining the following theorem,

$$(\phi_1*)^i = \Pi i. \text{ coefficient of } t^i \text{ in } T,$$

where

$$T = \phi_1 t + \phi_2 \frac{t^2}{1.2} + \phi_3 \frac{t^3}{1.2.3} + \dots, \quad (A)$$

a relation which may be expressed by means of the identity

$$e^{t\phi_1*} = (e^T)*\dagger, \quad (A) \text{ bis}$$

which important equation has been previously noticed by Professor Cayley under a somewhat less general form.

With the exception of noticing that  $(\phi_1*)^r$  and  $(\phi_1*)^s$  are commutable symbols by virtue of their definition, *i. e.* that

$$(\phi_1*)^r (\phi_1*)^s = (\phi_1*)^s (\phi_1*)^r,$$

I am not at present aware that this theory of derivation when the form of  $\phi$  is left undetermined presents much that is remarkable. Very different, however, is the case when we proceed to give to  $\phi$  the particular form in which it enters into the calculus of invariants: a most surprising and unexpected system of relations then springs up between the various orders of operators; and a vast and inexhaustible theory opens out before us, of which I want leisure to be able to do more than briefly notice one or two salient features.

Let

$$E_1 = a \frac{d}{db} + 2b \frac{d}{dc} + 3c \frac{d}{dd} + \dots + a' \frac{d}{db'} + 2b' \frac{d}{dc'} + \dots + a'' \frac{d}{db''} + \dots,$$

and similarly

$$\psi*\phi* = (\phi\psi)* + [\psi*\phi]*.$$

Hence if two operators  $\phi*$ ,  $\psi*$  are commutable, so, in respect to the symbol of operation  $*$ , are the two operands  $\phi$ ,  $\psi$ .

The force of the bracket explains itself. This wonderful symbol has the faculty of extending itself without ambiguity to every possible development, however new, of mathematical language. It is susceptible only of a metaphysical definition as signifying the exercise, with regard to its content, of that faculty of the human mind whereby a multitude is capable of being regarded as an individual, or a complex as a monad. In a word, it is the symbol of individuality and unification.

† Thus, *ex. gr.*, let  $\phi_1$  represent  $x \frac{d}{dx}$ , then  $\phi_2, \phi_3, \dots$  will be all equal to  $\phi_1$ ; accordingly  $T = (e^t - 1)\phi_1$ , and the formula in the text becomes

$$e^{\left(t x \frac{d}{dx}\right)*} = (e^{(e^t - 1)x \frac{d}{dx}})*,$$

a remarkable formula of expansion.

i. e.

$$= \Sigma \left( a \frac{d}{db} + 2b \frac{d}{dc} + 3c \frac{d}{dd} \dots \right).$$

Then if I be any function of the coefficients  $a, b, c, \dots; a', b', c', \dots$  in the algebraic forms  $(a, b, c, \dots)(x, 1)^p; (a', b', c', \dots)(x, 1)^p \dots$ , and  $I_1$  is what I becomes when we substitute for  $a, b, c, \dots; a', b', c', \dots$ , the values which these coefficients assume when  $x+h$  is written in place of  $h$ , it is, or ought to be, well known that

$$I_1 = I + E_1 * I h + (E_1 *)^2 I \frac{h^2}{1 \cdot 2} + (E_1 *)^3 I \frac{h^3}{1 \cdot 2 \cdot 3} + \dots$$

Here

$$E_1 * E_1 = 2 \Sigma \left( a \frac{d}{dc} + 3b \frac{d}{dd} + 6c \frac{d}{de} + \dots \right),$$

$$E_1 * E_1 * E_1 = 2 \cdot 3 \Sigma \left( a \frac{d}{dd} + 6b \frac{d}{de} + \dots \right),$$

$$\dots = \dots;$$

it will therefore become convenient slightly to depart from the notation applied to the general form  $\phi$ , and to write

$$E_1 = \Sigma \left( a \frac{d}{db} + 2b \frac{d}{dc} + \dots \right),$$

$$E_2 = \Sigma \left( a \frac{d}{dc} + 3b \frac{d}{dd} + \dots \right),$$

$$\dots$$

$$E_n = \Sigma \left( a \frac{d}{da_n} + nb \frac{d}{db_n} + n \frac{n+1}{2} \frac{d}{dc_n} + \dots \right);$$

where  $a_n, b_n, c_n, \dots$  are used to express the elements  $n$ , steps more advanced than  $a, b, c, \dots$  respectively; we have then by the general theorem

$$e^{tE_1*} = (e^T)*, \quad \dots \quad (B)$$

where T now takes the form

$$E_1 t + E_2 t^2 + E_3 t^3 + \dots$$

I propose to give to the E series of operators the general name of Extensor Operators, or simply Extensors.

The first remarkable, I may say marvellous, property of these extensors is, that they form a sort of closed group; *i. e.* any two algebraical functions whatever of the extensors regarded as algebraic functions of the quantities  $a, b, c, \dots; \frac{d}{db}, \frac{d}{dc}, \dots$  being

used as new operators and applied in succession to the same operand, the result is the same as if *some single third algebraical function* of the extensors had operated alone on this operand. The second great fact is, that the order in which the above-described operations take place is indifferent, *i. e.* that the two operators above described are commutable; in other words, we have always

$$\left. \begin{aligned} \theta(E_1, E_2, E_3, \dots) * \psi(E_1, E_2, E_3, \dots) * \\ = \Omega(E_1, E_2, E_3, \dots) * \\ = \psi(E_1, E_2, E_3, \dots) * \theta(E_1, E_2, E_3, \dots) * \end{aligned} \right\} \dots \quad (C)$$

Thus, *ex. gr.*,

$$E_\mu^i * E_\mu^j * = F(E_\mu, E_{2\mu}) * = E_\mu^j * E_\mu^i *,$$

where, writing  $m = \frac{\Pi(2\mu)}{(\Pi\mu)^2}$ ,  $F$  represents the *quasi* hypergeometric series,

$$\left. \begin{aligned} E_\mu^{i+j} + i \cdot j \cdot m E_\mu^{i+j-2} \cdot E_{2\mu} + \frac{i(i-1)j(j-1)}{1 \cdot 2} m^2 E_\mu^{i+j-4} \cdot E_{2\mu}^2 \\ + \frac{i(i-1)(i-2)j(j-1)(j-2)}{1 \cdot 2 \cdot 3} m^3 \cdot E_\mu^{i+j-6} E_{2\mu}^3 + \dots \end{aligned} \right\} \quad (D)$$

and  $E_\mu^i * E_\nu^j *$  will be expressible under a form *quam proximè* analogous. My immediate intention in this brief notice being merely to call attention to the surprising properties of these functions, I shall conclude with adding a slight extension of theorem (B) above given, *viz.*

$$e^{tE_1*} = (e^T)*.$$

This may be regarded as a particular case of a more general theorem which I have discovered, *viz.*

$$E_1^j * e^{tE_1*} = e^{tE_1*} E_1^j * = \left( \left( \frac{dT}{dt} \right)^j e^T \right) *,$$

a theorem which, with a simple change in the coefficients of  $T$ , may be extended to the still more general form  $E_\omega^j * e^{tE_\omega*}$ , so as to give a simple solution of the equation

$$X* = (E_\omega^*)^i E_\omega^j *,$$

where  $X$  is a form to be determined as an algebraical function of  $E_\omega$ ,  $E_{2\omega}$ ,  $E_{3\omega}$ , &c. . . .

The cardinal problem to be solved in the theory of extensors is the determination of  $\Omega$  in formula (C), where  $\psi$  and  $\theta$  are any given functional forms.



In the further development of this theory, it will probably be found expedient to suppose the number of the elements,  $a, b, c, \dots, j, k, l$ , to become finite, which will limit the number of the derived extensors, and to study the mutual reactions of the correlated series of extensors (with their derivatives), which we may characterize respectively as the E and II series, where

$$E_1 = \Sigma \left( a \frac{d}{db} + 2b \frac{d}{dc} + \dots \right),$$

$$H_1 = \Sigma \left( l \frac{d}{dk} + 2k \frac{d}{dl} + \dots \right).$$

Either of the above two primitive forms (as it is the imperishable glory of Professor Cayley to have discovered\*) is sufficient in itself for testing the nature of every invariant satisfying the necessary and obvious condition of weight, and for deducing the complete form of a covariant from either of its extreme terms; which latter consideration affords, I think, a sufficient ground for the name (of some kind or another so much needed) *Extensors*, which I propose to give to these too-long-suffered-to-remain anonymous test operators and their derivatives.

K, Woolwich Common,  
November 13, 1866.

### Postscript.

Since the above was sent to press it has occurred independently to Professor Cayley, to whom I had communicated a sketch of the theory, and to myself, that the general conclusions contained in the text above would remain valid for a much more general class of operants than those there defined; and there can be little or no doubt that such is the case for all operants *lineo-linear* in a set of elements  $a, b, c, \dots$ , and their præ-reciprocals  $\frac{d}{da}, \frac{d}{db}, \frac{d}{dc}, \dots$ . Moreover a material improvement in the nomenclature has suggested itself, which I proceed to explain. It is most important in this theory to be able to distinguish between the corpus or root of an operator viewed as a function and the operator itself, and to be in possession of a single

\* But this magnificent discovery, whereby the determination of the number of fundamental invariants to a binary quantic of a given degree is reduced to a problem in the partition of numbers, it is but justice to M. Hermite to state, took its rise in that great analyst's discovery of the cetodecimal invariant of the binary quintic. So long as the existence of this fourth invariant to that form was unsuspected, it must have remained impossible to conjecture the sufficiency of the single partial differential equation-test.

name for the former. Accordingly, in conformity with the general terminology of the new algebra, I propose to substitute the name of Protractor for Extensor to signify the *operator*, so as to be able to use the word Protractant to signify the *corpus*. Also I shall give the analogous names of Pertractant† and Pertractor—the former to the lineo-linear function above referred to, the latter to this function *energized*, i. e. converted into an operator by the addition of the asterisk \*, the symbol of operative power.

We thus start with a pertractant  $P_1$  which is *energized* into a pertractor,  $P_1*$ ; with this latter we continue to operate any number of times upon the original pertractant, and obtain a succession of new derived pertractants, into which it appears at present to be convenient, for the sake of uniformity, to introduce the numerical divisors 2, 3, 4, . . . , so that we may define  $P_{n+1}$ , the *n*th derivative pertractant, as equal to  $\frac{(P_1^*)^n P_1}{\Pi(n+1)}$ .

We thus obtain a series of pertractants,  $P_1, P_2, P_3, \dots$ , which may be termed the primitive and prime derivative pertractants of the family.

Again, we may form any algebraical function of the primitive and its prime derivatives, and such function may be termed a compound derivative of the family; this in its turn, by the addition of the symbol of operative power, may be energized into a pertractive operator, which, containing only a single asterisk, is to be regarded as a simple or single derived pertractor, although its corpus is a compound derivative.

The first leading proposition of the theory is, that all operators so formed are *commutable*, so that, being subject to the laws of algebraical operation, they may themselves be made the subjects of algebraical functions. The second great proposition is, that any such function of one or more pertractors is reducible to the form of a *single pertractor*, i. e. is an energized function of the prime pertractants  $P_1, P_2, P_3, \dots$ .

The theorems that have been stated concerning protractants and protractors will continue to subsist for the much more general class of pertractors and pertractants. Thus, *ex. gr.*, theorem (D) in the text above, when we take  $\mu=1$ , becomes

$$E_1^i * E_1^j = E_1^{i+j} + i \cdot j E_1^{i+j-2} (2E_2) + \frac{i(i-1)j(j-1)}{1 \cdot 2} E_1^{i+j-4} (2E_2)^2 + \dots$$

† Thus the “*Universal Mixed Concomitant*”  $x \frac{d}{dx} + y \frac{d}{dy} + z \frac{d}{dz} + \dots$  is of the genus Pertractant.

Mr. Cayley verifies this theorem when for  $E_1$ , the leading protractant, we substitute  $P_1$ , a pertractant, as follows. Take only a single element  $x$  and its symbolical reciprocal  $\frac{d}{dx}$ , so that

$$P_1 = x \frac{d}{dx}; \text{ then } P_2 = \frac{1}{2}P, \text{ and } P_1^i \cdot P_1^j = \left( x^i \left( \frac{d}{dx} \right)^i \right) * \left( x^j \frac{d}{dx} \right)^j$$

is easily seen to be

$$\begin{aligned} & P_1^{i+j} + \frac{j}{1} P_1^{i+j-1} + \frac{i(i-1)j(j-1)}{1 \cdot 2} P_1^{i+j-2} + \dots \\ &= P_1^{i+j} + \frac{i \cdot j}{1} P_1^{i+j-2} (2P_2) + \frac{i(i-1)j(j-1)}{1 \cdot 2} P_1^{i+j-4} (2P_2)^2 + \dots \end{aligned}$$

as before.

But I find that the theory admits of a still further and most important extension. Thus far we have been dealing with operants and operators derived from a single one of the former. But we may easily form a set of two or more, say  $k$  pertractants, *i. e.* functions lineo-linear in  $a, b, c$ ; ...  $\frac{d}{da}, \frac{d}{db}, \frac{d}{dc}$  ... commutable *inter se*†; these being *energized* into

† This imports into the subject a beautiful theory of commutable matrices. In the case of two letters we have two types of commutable pertractors, from which all the rest may be derived by the laws of pertraction stated in the text. These two fundamental systems are,

$$(1) \quad x\delta_x; \quad y\delta_y.$$

$$(2) \quad \begin{pmatrix} a, b \\ c, d \end{pmatrix} (x, y)(\delta_x, \delta_y); \quad x\delta_x + y\delta_y.$$

In the case of three letters, the four following types of commutable systems present themselves:—

$$(1) \quad x\delta_x; \quad y\delta_y; \quad z\delta_z.$$

$$(2) \quad \begin{pmatrix} a, b \\ c, d \end{pmatrix} (x, y)(\delta_x, \delta_y); \quad x\delta_x + y\delta_y; \quad z\delta_z.$$

$$(3) \quad ax\delta_y + by\delta_z + cz\delta_x; \quad \frac{1}{a}y\delta_x + \frac{1}{b}z\delta_y + \frac{1}{c}x\delta_z.$$

$$(4) \quad \begin{pmatrix} a, b, c \\ d, e, f \\ g, h, k \end{pmatrix} (x, y, z)(\delta_x, \delta_y, \delta_z); \quad x\delta_x + y\delta_y + z\delta_z.$$

Whether the above four systems are independent, and whether they constitute an exhaustive enumeration in the case of three letters, I have not yet had time to ascertain.

The reader will please to bear in mind that any linear function of the terms in each system, or of them and their derivatives, is commutable with those terms themselves; thus, *ex. gr.*, the last system but one is quite as extensive as if we included in it

$$\lambda ax\delta_y + \lambda by\delta_x + \lambda cz\delta_x + \frac{\mu}{a}y\delta_x + \frac{\mu}{b}z\delta_y + \frac{\mu}{c}x\delta_z + \sqrt{x}\delta_x + \sqrt{y}\delta_y + \sqrt{z}\delta_z,$$

operators which are made to act on the functions themselves, will give rise to  $r \cdot \frac{r+1}{2}$  first derivatives, which, energized in their turn, will be commutable *inter se* and with the original operators: the derivatives of the next order enjoying the same properties will be  $r \cdot \frac{r+1}{2} \cdot \frac{r+2}{3}$ , and so on. Thus, as before, we obtain the *prime* pertractive derivants of various orders, with the difference that there are now several of such prime derivants belonging to each order. Any function of these gives rise to a compound-pertractive derivant, the number of which is of course unlimited; these may be energized into operators, subject *inter se* to all the laws of algebraical operation, and any function of one or more of such compound-pertractive derivators will be equivalent to some single derivator belonging to the same family. In a word, the theory may be extended from the case of *Monocephalous* to that of *Polycephalous* pertractive functions and operators and their derivatives.

I will conclude for the second time with the statement of an expansion in a series which, as far as I have been able to ascertain, is new to writers on the differential calculus, to which I was led by applying the symbolical equation previously given in a footnote to the *operand*  $a^x$ . The equation in question may be written as follows:

$$e^{(ta \frac{d}{da})^*} = (e^{(et-1)^a} \frac{d}{da})^* ;$$

from this I have been able to deduce by a mental calculation, the steps of which I am unable to recall, a development which would be exceedingly difficult to obtain from the method of Maclaurin's theorem. I find

$$\begin{aligned} (-\log(1-x))^n &= x^n + S_{n,1} \frac{x^{n+1}}{n+1} + S_{n+1,2} \frac{x^{n+2}}{(n+1)(n+2)} \\ &+ S_{n+2,3} \frac{x^{n+3}}{(n+1)(n+2)(n+3)} + \dots, \end{aligned}$$

where in general  $S_{i,j}$  signifies the sum of the  $\frac{i \cdot (i-1) \dots (i-j+1)}{1 \cdot 2 \dots j}$

products of the combinations of the numbers  $1, 2, 3, \dots, i$ , taken  $j$  and  $j$  together. This development may be easily verified

in which it will be noticed that the three last terms may be obtained (to a constant factor *près*) by operating with the sum of the three first upon the sum of the three middle terms, or *vice versâ*.



inductively by aid of the identical equation

$$\frac{d}{dx} (\log (1-x))^n = - \frac{n (\log (1-x))^{n-1}}{1-x},$$

combined with the relation

$$\begin{aligned} S_{n+j-1,j} &= S_{n+j-2,j} + j S_{n+j-2,j-1} \dagger \\ &= S_{n+j-2,j} + j S_{n+j-3,j-1} + j(j-1) S_{n+j-4,j-2} \\ &\quad + j(j-1)(j-2) S_{n+j-5,j-3} + \&c. \end{aligned}$$

It is obvious that the coefficients of the powers of  $x$  in the above expansion must be all of them integral functions of  $n$ , and must also contain  $n$  in every term except the first; and when so expressed as integer functions of  $n$ , the result obtained on the supposition of  $n$  being a positive integer will continue to subsist for all values of  $n$ . From the first part of this statement, it follows that  $S_{i,j}$  may always be expressed under the form

$$((i+1)i \cdot (i-1) \dots (i-j+1)) \phi_{j-1}(i),$$

where  $\phi_{j-1}(i)$  is a quantic in  $i$  of the degree  $j-1$ .

Furthermore, if we suppose

$$\phi_{j-1}(i) = \frac{\psi_{j-1}(i)}{2^\alpha \cdot 3^\beta \cdot 5^\gamma \cdot 7^\delta \cdot 11^\epsilon \dots p^{\phi(p)} \dots},$$

$p$  being any prime number, and  $\psi$  a function of  $i$  of the degree  $(j-1)$  all whose coefficients are integer, and (consistently with this being the case) as small as they can be made, there is no difficulty in obtaining the value of  $\phi(p)$  under the following form,

$$\phi(p) = \sum_{\mu=\infty}^{\mu=0} E \left( \frac{j}{p-1} p^\mu \right) \dagger,$$

where, as usual, the symbol  $E$  signifies that *only* the integer part is to be preserved of the number upon which it acts. The value of the coefficient of  $i^{j-1}$  in  $\phi_{j-1}i$  is easily ascertained to be  $\frac{1}{(1 \cdot 2 \cdot 3 \dots j) 2^j}$ , and consequently the coefficient of  $i^{j-1}$  in  $\psi$  is

† The equation in differences  $S_{n,j} = S_{n-1,j} + j S_{n-1,j-1}$  gives an easy algorithm for calculating  $S_{n,j}$ , and shows *a priori* that it is divisible by  $(n+1)n \dots (n-j+1)$ .

‡ Consequently  $\phi(p)$ , the exponent of  $p$ , is always less than  $\frac{pj}{(p-1)^2}$ , and

*à fortiori* than  $\frac{j}{p-2}$ .

always an odd number, the number of times that 2 is contained in this denominator being

$$\sum_{\mu=0}^{\mu=j} E_{2^{\mu}}^j.$$

The maximum prime in the denominator of the fraction which expresses  $\phi_{j-1}(i)$  enters always as a simple factor, because, as we know by M. Bertrand's theorem, there is always a prime number included between  $q+1$  and  $2q+2$ . Consequently, supposing  $j$  to be  $2q$  or  $2q+1$ , since there exists a prime number  $p$  greater than  $q+1$ , and not greater than  $2q+1$ , this prime number will appear in the denominator of  $S_{n,j}$  with the exponent  $E\left[\frac{2q \text{ or } 2q+1}{p-1}\right]$ , i. e. unity.

Conversely, if by any means not founded on the above theorem we could ascertain this fact, we should be in possession of an entirely new proof of that celebrated theorem. It is perhaps also worthy of a passing notice, that  $(-)^j \cdot \phi_{j-1}(j-1)$  may easily be proved to be equal to the coefficient of  $t^j$  in  $\log \log(1+t) - \log t$ .

I have calculated the values of  $s_{i,1}$ ;  $s_{i,2}$ ;  $s_{i,3}$ ;  $s_{i,4}$ , which are as follows :

$$\frac{(i+1)i}{2}; \quad \frac{(i+1)i(i-1)}{2^3 \cdot 3} (3i+2); \quad \frac{(i+1)i(i-1)(i-2)}{2^4 \cdot 3} i(i+1);$$

$$\frac{(i+1)i(i-1)(i-2)(i-3)}{2^4 \cdot 3^2 \cdot 5} (15i^3 - 15i^2 + 10i - 8) \dagger.$$

† And more generally if

$$S_{n+j-1,j} = ((n+j)(n+j-1) \dots n) (C_j n^{j-1} + C_{j-1} n^{j-2} + \dots + C_1),$$

$$(-)^j C_{\omega} = \frac{C1}{\Pi \omega} \cdot \text{coefficient of } t^j \text{ in } \left( \log \left( \frac{\log(1+t)}{t} \right) \right)^{\omega}.$$

‡ In his great and most useful work on the Calculus (p. 264), Professor De Morgan has applied Arbogast's method to the expansion of  $(\log(1+x))^n$ , and worked out his results completely as far as the coefficients of  $x^4$  inclusive. His  $\frac{C}{n}, \frac{E}{n}, \frac{F}{n}$ , when  $i-1, i-2, i-3$  are substituted in these quotients for  $n$ , become identical with the *non-trivial*, or so to say outstanding factors in my  $S_{i,2}$ ;  $S_{i,3}$ ;  $S_{i,4}$  respectively.

I have since calculated the same factors for  $S_{i,5}$ ,  $S_{i,6}$  corresponding to Professor De Morgan's  $\frac{G}{n}, \frac{H}{n}$ , when  $n$  is replaced by  $i-4, i-5$  respectively.

The calculations are rather laborious, extending in the latter case to 8 places of digits; but comparatively very small numbers appear in the final expressions. For  $S_{i,5}$  I find the outstanding factor takes the ex-

The following observation from Professor Cayley will be found interesting:—

“In the case of two variables, if

$$P_1 = (ax + by) \frac{d}{dx} + (cx + dy) \frac{d}{dy},$$

then in the notation of matrices,

$$P_1 = \begin{Bmatrix} a, & b \\ c, & d \end{Bmatrix} (x, y) \left( \frac{d}{dx}, \frac{d}{dy} \right),$$

$$P_2 = \frac{1}{2} \begin{Bmatrix} a, & b \\ c, & d \end{Bmatrix}^2 (x, y) \left( \frac{d}{dx}, \frac{d}{dy} \right),$$

$$P_3 = \frac{1}{6} \begin{Bmatrix} a, & b \\ c, & d \end{Bmatrix}^3 (x, y) \left( \frac{d}{dx}, \frac{d}{dy} \right);$$

whence also

$$P * P_2 = P_2 * P_1 = \frac{1}{2} \begin{Bmatrix} a, & b \\ c, & d \end{Bmatrix}^3 (x, y) \left( \frac{d}{dx}, \frac{d}{dy} \right) = 3P_3,$$

which accords with your theorem,

$$E_1 * E_2 * = E_2 * E_1 * = E_1 E_2 * + 3E_3 *."$$

ceedingly simple form

$$\frac{i(i+1)(3i^2-i-6)}{2^8 \cdot 3^2 \cdot 5},$$

and for  $S_{i,6}$  the form

$$\frac{63i^5 - 315i^3 + 224i^2 + 140i - 96}{2^{10} \cdot 3^3 \cdot 5 \cdot 7}.$$

I think there can be little doubt that the outstanding factor in  $S_{i,j}$  becomes more liable to decomposition into algebraical factors in proportion as the number  $j+1$  becomes more separable into numerical factors, *i. e.* in proportion as  $j+1$  contains a smaller number of distinct prime factors. For this reason I purpose calculating  $S_{i,7}$ ,  $S_{i,8}$  against the appearance of the next Number of the Magazine. The nature of the roots, as regards being real or imaginary in the equation  $S_{i,j}=0$ , is also probably well deserving of study. It is worthy of notice that in each of the irreducible factors of  $S_{i,j}$  for the values of  $j$  above considered, the coefficients are composed exclusively of the prime factors which enter into  $j+1$ . It is hardly

necessary to observe that the quantities  $\frac{S_{n+j-1,j}}{(n+1)(n+2)\dots(n+j)}$ , when expressed in a rational integral form, are the coefficients of the powers of  $x$  in the series for  $[\log(1+x)]^a$ , when  $n$  is regarded no longer as a positive integer, but as an arbitrary variable.

I have taken the liberty of writing in the above  $\frac{d}{dx}, \frac{d}{dy}$  for  $\delta_x, \delta_y$ , and P for  $\delta$  in the original. It will be useful to bear in mind that in any operator such as  $E_1^*$  or  $E_2^*$ , the asterisk forms an integral part of the symbol†. Thus  $E_1^* E_2^*$ , if we choose, may be written under the form of  $E_1^*$  multiplied by  $E_2^*$ , i. e.  $(E_1^*) \times (E_2^*)$ , where the cross is the sign of ordinary algebraical multiplication.

#### LXIV. *Proceedings of Learned Societies.*

##### ROYAL SOCIETY.

[Continued from p. 393.]

June 21, 1866.—Lieutenant-General Sabine, President, in the Chair.

THE following communication was read:—

“On the Expansion by Heat of Metals and Alloys.” By A. Matthiessen, F.R.S.

In a paper “On the Expansion by Heat of Water and Mercury”‡, a method of determining the expansion of bodies is described, by which good results can be obtained with comparatively small quantities of the substances to be experimented with. This method, that of weighing the body in water at different temperatures, has been employed for the present research. The results obtained are given in the following Tables:—

† The operant, sign of operation, and operand form a triad somewhat analogous to the subject, copula, and predicate of the logicians; and as in the admirable new school of philosophical grammar the copula is for certain purposes incorporated with the predicate, so *ex converso* in this system the sign of operation is taken up by the operant; but, herein advantageously differing from the practice of the grammarians alluded to, the combination assumes a distinct name from its leading element and is styled an operator.

I ought to mention that my information in this matter is derived from the statements which have appeared in the public prints, and not from a direct study of that wonderful manual of the quintessence of grammar so unpretendingly ushered into the world as a *primer*, but which, whatever name it goes by, can hardly fail to bring about a philosophical revival of the intellect of the rising generation of Englishmen. I wait for a favourable opportunity of leisure to address the full energies of my mind to the invigorating and congenial task of mastering its subtle differentiations and profound and arduous abstractions.

‡ Phil. Trans. 1866, part I.



TABLE I.—Formulæ for the Correction of the Cubical Expansion by Heat of the Metals.

Cadmium.....	$V_t = V_0 (1 + 10^{-4} \times 0.8078t + 10^{-6} \times 0.140t^2)^*$ .
Zinc.....	$V_t = V_0 (1 + 10^{-4} \times 0.8222t + 10^{-6} \times 0.0706t^2)$ .
Lead.....	$V_t = V_0 (1 + 10^{-4} \times 0.8177t + 10^{-6} \times 0.0222t^2)$ .
Tin.....	$V_t = V_0 (1 + 10^{-4} \times 0.6100t + 10^{-6} \times 0.0789t^2)$ .
Silver.....	$V_t = V_0 (1 + 10^{-4} \times 0.5426t + 10^{-6} \times 0.0405t^2)$ .
Copper.....	$V_t = V_0 (1 + 10^{-4} \times 0.4163t + 10^{-6} \times 0.0555t^2)$ .
Gold.....	$V_t = V_0 (1 + 10^{-4} \times 0.4075t + 10^{-6} \times 0.0336t^2)$ .
Bismuth.....	$V_t = V_0 (1 + 10^{-4} \times 0.3502t + 10^{-6} \times 0.0446t^2)$ .
Palladium.....	$V_t = V_0 (1 + 10^{-4} \times 0.3032t + 10^{-6} \times 0.0280t^2)$ .
Antimony.....	$V_t = V_0 (1 + 10^{-4} \times 0.2770t + 10^{-6} \times 0.0397t^2)$ .
Platinum.....	$V_t = V_0 (1 + 10^{-4} \times 0.2554t + 10^{-6} \times 0.0104t^2)$ .

TABLE II.—Formulæ for the Correction of the Linear Expansion by Heat of the Metals.

Cadmium.....	$L_t = L_0 (1 + 10^{-4} \times 0.2693t + 10^{-6} \times 0.0466t^2)$ .
Zinc.....	$L_t = L_0 (1 + 10^{-4} \times 0.2741t + 10^{-6} \times 0.0234t^2)$ .
Lead.....	$L_t = L_0 (1 + 10^{-4} \times 0.2726t + 10^{-6} \times 0.0074t^2)$ .
Tin.....	$L_t = L_0 (1 + 10^{-4} \times 0.2033t + 10^{-6} \times 0.0263t^2)$ .
Silver.....	$L_t = L_0 (1 + 10^{-4} \times 0.1809t + 10^{-6} \times 0.0135t^2)$ .
Copper.....	$L_t = L_0 (1 + 10^{-4} \times 0.1481t + 10^{-6} \times 0.0185t^2)$ .
Gold.....	$L_t = L_0 (1 + 10^{-4} \times 0.1358t + 10^{-6} \times 0.0112t^2)$ .
Bismuth.....	$L_t = L_0 (1 + 10^{-4} \times 0.1167t + 10^{-6} \times 0.0149t^2)$ .
Palladium.....	$L_t = L_0 (1 + 10^{-4} \times 0.1011t + 10^{-6} \times 0.0093t^2)$ .
Antimony.....	$L_t = L_0 (1 + 10^{-4} \times 0.0923t + 10^{-6} \times 0.0132t^2)$ .
Platinum.....	$L_t = L_0 (1 + 10^{-4} \times 0.0850t + 10^{-6} \times 0.0035t^2)$ .

TABLE III.—Formulæ for the Correction of the Cubical Expansion by Heat of the Alloys.

$\text{Sn}_1 \text{ Pb}$	$V_t = V_0 (1 + 10^{-4} \times 0.6200t + 10^{-6} \times 0.0988t^2)$ .
$\text{Pb}_1 \text{ Sn}$	$V_t = V_0 (1 + 10^{-4} \times 0.8087t + 10^{-6} \times 0.0332t^2)$ .
$\text{Cd Pb}$	$V_t = V_0 (1 + 10^{-4} \times 0.9005t + 10^{-6} \times 0.0133t^2)$ .
$\text{Sn}_4 \text{ Zn}$	$V_t = V_0 (1 + 10^{-4} \times 0.6377t + 10^{-6} \times 0.0807t^2)$ .
$\text{Sn}_6 \text{ Zn}$	$V_t = V_0 (1 + 10^{-4} \times 0.6236t + 10^{-6} \times 0.0822t^2)$ .
$\text{Bi}_{14} \text{ Sn}$	$V_t = V_0 (1 + 10^{-4} \times 0.3793t + 10^{-6} \times 0.0271t^2)$ .
$\text{Bi Sn}_5$	$V_t = V_0 (1 + 10^{-4} \times 0.4997t + 10^{-6} \times 0.0101t^2)$ .
$\text{Bi}_{21} \text{ Pb}$	$V_t = V_0 (1 + 10^{-4} \times 0.3868t + 10^{-6} \times 0.0218t^2)$ .
$\text{Bi Pb}_2$	$V_t = V_0 (1 + 10^{-4} \times 0.8462t + 10^{-6} \times 0.0159t^2)$ .
$\text{Cu} + \text{Zn}$ (71 p. c. Cu)	$V_t = V_0 (1 + 10^{-4} \times 0.5161t + 10^{-6} \times 0.0558t^2)$ .
$\text{Au Sn}_2$	$V_t = V_0 (1 + 10^{-4} \times 0.3944t + 10^{-6} \times 0.0289t^2)$ .
$\text{Au}_2 \text{ Sn}_7$	$V_t = V_0 (1 + 10^{-4} \times 0.4165t + 10^{-6} \times 0.0263t^2)$ .
$\text{Ag}_4 \text{ Au}$	$V_t = V_0 (1 + 10^{-4} \times 0.5166t)$ .
$\text{Ag Au}$	$V_t = V_0 (1 + 10^{-4} \times 0.4916t)$ .
$\text{Ag Au}_4$	$V_t = V_0 (1 + 10^{-4} \times 0.3115t + 10^{-6} \times 0.1185t^2)$ .
$\text{Ag} + \text{Pt}$ (66.6 p. c. Ag)	$V_t = V_0 (1 + 10^{-4} \times 0.4246t + 10^{-6} \times 0.0322t^2)$ .
$\text{Au} + \text{Cu}$ (66.6 p. c. Au)	$V_t = V_0 (1 + 10^{-4} \times 0.4015t + 10^{-6} \times 0.0642t^2)$ .
$\text{Ag} + \text{Au}$ (36.1 p. c. Ag)	$V_t = V_0 (1 + 10^{-4} \times 0.4884t + 10^{-6} \times 0.0552t^2)$ .
$\text{Ag} + \text{Au}$ (71.6 p. c. Ag)	$V_t = V_0 (1 + 10^{-4} \times 0.4413t + 10^{-6} \times 0.0130t^2)$ .

\* I have employed this method of writing the formulæ to prevent mistakes

TABLE IV.—Formulæ for the Correction of the Linear Expansion by Heat of the Alloys.

Sn <sub>4</sub> Pb	$L_t = L_0 (1 + 10^{-4} \times 0.2066t + 10^{-6} \times 0.0329t^2).$
Pb <sub>4</sub> Sn	$L_t = L_0 (1 + 10^{-4} \times 0.2696t + 10^{-6} \times 0.0111t^2).$
Cd Pb	$L_t = L_0 (1 + 10^{-4} \times 0.3002t + 10^{-6} \times 0.0044t^2).$
Sn <sub>4</sub> Zn	$L_t = L_0 (1 + 10^{-4} \times 0.2126t + 10^{-6} \times 0.02691t^2).$
Sn <sub>5</sub> Zn	$L_t = L_0 (1 + 10^{-4} \times 0.2079t + 10^{-6} \times 0.0274t^2).$
Bi <sub>4</sub> Sn	$L_t = L_0 (1 + 10^{-4} \times 0.1264t + 10^{-6} \times 0.0090t^2).$
Bi <sub>4</sub> Sn <sub>2</sub>	$L_t = L_0 (1 + 10^{-4} \times 0.1666t + 10^{-6} \times 0.0034t^2).$
Bi <sub>4</sub> Pb	$L_t = L_0 (1 + 10^{-4} \times 0.1293 + 10^{-6} \times 0.0073t^2).$
Bi Pb <sub>2</sub>	$L_t = L_0 (1 + 10^{-4} \times 0.2821 + 10^{-6} \times 0.0053t^2).$
Cu + Zn (71 p. c. Cu)	$L_t = L_0 (1 + 10^{-4} \times 0.1720t + 10^{-6} \times 0.0086t^2).$
Au Sn <sub>2</sub>	$L_t = L_0 (1 + 10^{-4} \times 0.1315t + 10^{-6} \times 0.0096t^2).$
Au <sub>2</sub> Sn <sub>7</sub>	$L_t = L_0 (1 + 10^{-4} \times 0.1388t + 10^{-6} \times 0.0088t^2).$
Ag Au	$L_t = L_0 (1 + 10^{-4} \times 0.1722t).$
Ag Au	$L_t = L_0 (1 + 10^{-4} \times 0.1638t).$
Ag Au <sub>4</sub>	$L_t = L_0 (1 + 10^{-4} \times 0.1038t + 10^{-6} \times 0.0395t^2).$
Ag + Pt (66.6 p. c. Ag)	$L_t = L_0 (1 + 10^{-4} \times 0.1415t + 10^{-6} \times 0.0107t^2).$
Au + Cu (66.6 p. c. Au)	$L_t = L_0 (1 + 10^{-4} \times 0.1338t + 10^{-6} \times 0.0214t^2).$
Ag + Cu (36.1 p. c. Ag)	$L_t = L_0 (1 + 10^{-4} \times 0.1628t + 10^{-6} \times 0.0182t^2).$
Ag + Cu (71.6 p. c. Ag)	$L_t = L_0 (1 + 10^{-4} \times 0.1471t + 10^{-6} \times 0.0433t^2).$

From the above the following conclusion is drawn—namely, that just as it may be said that the *specific gravity of an alloy is approximately equal to the mean specific gravities of the component metals*, so also from the foregoing we may deduce that the *volume which an alloy will occupy at any temperature between 0° and 100° is approximately equal to the mean of the volumes of the component metals at the same temperature*, or, in other words, *the cubical or linear coefficients of expansion by heat of an alloy between 0° and 100° are approximately equal to the mean of the cubical or linear coefficients of expansion by heat of the component metals*.

## GEOLOGICAL SOCIETY.

[Continued from p. 234.]

November 7, 1866.—Prof. A. C. Ramsay, LL.D., F.R.S.,  
Vice-President, in the Chair.

The following communications were read:—

1. "On some remains of large Dinosaurian Reptiles from the Stormberg Mountains, South Africa. By Prof. T. H. Huxley, F.R.S., V.P.G.S.

The specimen more particularly described in this paper is a portion of a right femur,  $25\frac{1}{2}$  inches long; so that the entire femur may be safely assumed to have exceeded 30 inches in length. The peculiar form of the bone, and the characters and position of the trochanters, leave no doubt of the Dinosaurian affinities of the reptile to which it belonged, which must have been comparable in

in the number of the zeros. I have also preferred keeping the exponents constant, adding instead of altering them, a zero after the decimal point when required.

point of size to its near allies, the *Megalosaurus* and the *Iguanodon*. To the former of these it possesses the closest affinity, but differs in the proportional size and form of its trochanters, and in its much heavier proportions; and the author proposes for it the name *Euskelosaurus Browni*.

A portion of the distal end of a femur indicating another genus of large-sized Dinosaurian reptiles was also described, the characters yielded being sufficient to prove that it belongs to another genus than *Euskelosaurus*.

The discovery of these remains in the Stormberg rocks was stated to be by no means decisive of their geological relations, as Dinosaurian reptiles lived throughout the Mesozoic period, and may have existed during the Permian; but it is interesting to observe that the Stormberg rocks conformably overlies the Karoo beds, which have yielded the Dicynodonts and so many other remarkable Reptiles and Labyrinthodonts.

2. "Additional Notes on the grouping of the rocks of North Devon and West Somerset." By J. Beete Jukes, Esq., M.A., F.R.S., F.G.S.

Commencing with the country around Wiveliscombe, near which place Sir H. De la Beche had indicated an east and west fault of small extension on the maps of the Geological Survey, Mr. Jukes described the rocks of the district reaching from that place north-west to the Brendon Hills, and westwards to Dulverton, including the valley of the Tone, more to the south. From Dulverton he examined the country towards Simonsbath, and then, proceeding to Barnstaple, made traverses from that place to Challacombe and to Bittadon. Similarly, after examining the neighbourhood of Combe Martin, he proceeded along the north coast in an easterly direction, through Countisbury, Porlock, and Dunster, and across the Williton valley to the Quantock Hills. The observations made during these several journeys were given in detail by the author; and the principal conclusions at which he had arrived in consequence were stated to be the following:—(1) There are three areas of Old Red Sandstone in this region, namely, *a*, The Quantock Hills; *b*, The Porlock, Minehead, and Dunster area; and *c*, The Morte Bay and Wiveliscombe ridge. (2) Each of these masses of Old Red Sandstone dips under a great mass of Carboniferous Slate. (3) The Coal-measures, the Carboniferous slate, and the Old Red Sandstone of Devon are contemporaneous with the Coal-measures, the Carboniferous Limestone, and the old Red Sandstone to the north of the Bristol Channel. (4) That if the great fault which the author believes to exist be proved to be absent, his other conclusions will not be altogether vitiated, for the red rocks of Porlock and Dunster may then be taken as the top of the true Old Red Sandstone lying underneath a great thickness of Carboniferous Slate. Mr. Jukes had also been able to construct a geological sketch map of North Devon in conformity with his views; and the paper concluded with a few notes explanatory of it.

LXV. *Intelligence and Miscellaneous Articles.*

NOTE ON THE USE OF THE DIFFERENTIAL GALVANOMETER IN  
EXPERIMENTS ON RADIANT HEAT. BY M. P. DESAINS.

THE sources of heat ordinarily used in investigating thermal radiation are never perfectly constant. Hence special precautions must be taken to exhibit with certainty the slight actions exerted on rays from these sources by causes not acting with any great energy. The difficulty is usually resolved by repeating a great number of times pairs of crossed observations—that is, those made alternately on the direct and on the modified pencil. This mode has the disadvantage of greatly prolonging the duration of the operations. In order to avoid this, which is frequently objectionable, De la Provostaye and I have used a totally different method, and one which gives the means of directly calculating the influence of variations of the source. But this method (*Comptes Rendus*, vol. xxxviii. p. 440) presupposes simultaneous observations, and hence the cooperation of two observers; it is, moreover, ill adapted to lecture-experiments. On the other hand, I have found that great certainty can be rapidly obtained in the most delicate thermoscopic observations, or manifestations, by using a kind of differential apparatus consisting essentially of a single source of heat, of two thermopiles, of a differential galvanometer, and, lastly, of a rheostat.

Each pile is connected with one of the two wires of the galvanometer, and the rheostat is interposed in one of the circuits. By this apparatus the actions of the two currents on the needle can be equalized, and thus kept at zero of the scale if they are in opposite directions.

Once obtained, equilibrium continues in spite of variations in the source; but if from any cause whatever the intensity of one of the radiations alters, the needle quits zero and sets in some other position. Both piles must be of the same construction if they are to be equally rapid in following the action of the heat. The difference indicated is finally the greater the more energetic are each of the currents which traverse the apparatus.

The first phenomenon I have investigated by the method I have described is that of the absorption of heat by transparent gases. To demonstrate in an easy and certain manner the very interesting results obtained by Magnus and Tyndall, I worked in the following manner:—

The source of heat is a lamp. The piles are at a distance of about 1.8 metre from the flame, to the centre of which their axes point, making with each other a considerable angle. Between the flame and each pile is placed a glass tube, about a metre in length by a decimetre in diameter, which can either be exhausted, or in which the air can be compressed to two or three atmospheres. Each of these tubes is closed at the two ends by thick transparent glass plates; its axis is in the prolongation of that of the corresponding pile.

The apparatus being thus arranged, one of the tubes is exhausted,



the other filled with well-dried coal-gas, the lamp lit, and by means of the rheostat the needle reduced to zero. Equilibrium being set up, the lamp is masked by means of a semicylindrical screen. The tube originally full is exhausted, the other filled with gas, and the screen removed, on which the needle begins to move. The deflection may easily amount to several degrees, and can be readily seen in projection.

The differential method is readily applied to the investigation of the rotations which the plane of polarization of a ray of heat undergoes under the action of a substance which has but little activity. The polarized ray is divided by a plate of calc-spar whose principal section makes an angle of  $45^\circ$  with the original plane of polarization. The two images have in that case the same intensity; one falls on the first pile, and the other on the other; and the needle is brought to zero. If, then, the original plane of polarization is deflected by a very small number of degrees ( $\alpha$ , for example), a difference is established between two images that were originally equal to one another and to I, the measure of which is

$$I[\sin^2(45 + \alpha) - \cos^2(45 + \alpha)] = I[4 \sin^2 45 \sin \alpha \cos \alpha] = I \sin 2\alpha.$$

The corresponding deviation might be still quite appreciable, while even with a more sensitive galvanometer the effect produced by the reappearance of the extinguished image would only have led to a much more feeble result. I may add that if, by means of a compensating plate or tube, the action of which can be readily estimated, the differential deflection whose relative value we have just calculated be made to disappear, we shall thereby obtain the value of the rotation originally produced.

I request permission from the Academy to communicate some attempts which I have made to transport into the domain of radiant heat a beautiful optical experiment devised by Biot.

When a ray of rectilinearly polarized light, in which, for instance, the vibrations are vertical, traverses at right angles to one of its faces a plate of glass untempered and suitably inclined, there is no special effect. If on emerging from the plate the ray passes through a plate of calc-spar whose section is parallel to the plane of polarization, it is totally refracted in the ordinary manner, the extraordinary image is zero; but if the plate be then made to vibrate longitudinally, and if the ray traverse it in the vicinity of a nodal point, the extraordinary image will reappear and continue as long as the vibratory motion continues. I have found that under these conditions the calorific image which is again formed may also be rendered visible.

The experiment is well made in the sun. It may also be made by the electrical lamp, and even with the radiation of incandescent lime. But it is produced very conveniently in a manner analogous to that above described—that is to say, using the vibration of a plate, not to cause the reappearance of the action of a pencil originally extinguished, but to produce a difference of intensity between two radiations whose actions on the piles of the differential apparatus had at first been made equal.

I must be permitted, in concluding this note, to thank M. Ruhmkorff for the kindness with which he has been pleased to place at my disposal, for the experiments described, a differential galvanometer of very great delicacy.—*Comptes Rendus*, October 22, 1866.

#### ON AQUEOUS VAPOUR AND SOLAR RADIATION.

[Extract of a Letter from M. Soret to Prof. Tyndall.]

During the past summer I have made some experiments on solar radiation. The bulb of a thermometer was placed in a cavity surrounded by ice, in order to prevent any agitation of the air, and to preserve the surrounding temperature constant. The solar rays fell directly on the bulb of the thermometer, which was first varnished and then coated with lampblack. In two comparative experiments made within a few days at Geneva and Bologna, the most powerful radiation was obtained at Geneva, although at Bologna the heavens were visibly *purser*. The result appears to me to support your views regarding the aqueous vapour of the air; for the tension of aqueous vapour at Bologna was 10·7, while at Geneva it was only 6·33. I have, however, made only one observation, my thermometer having been broken in returning. The single fact is not sufficient to enable me to draw a certain conclusion.

L. SORET.

Geneva, Nov. 13, 1866.

#### ON THE INFLUENCE OF THE EARTH'S ROTATION ON THE DEVIATION OF PROJECTILES FROM RIFLED CANNON. BY M. MARTIN DE BRETTE.

The distinguished geometrician Poisson treated this question in 1837 for the case of spherical projectiles, and has drawn the following conclusions:—

(1) The ranges vary with the azimuths of the plane of firing, but between very narrow limits; for the greatest variation would be two decimetres for a range of 1800 metres in firing from a mortar. It would be still less in firing point blank; so that, practically, the influence of the azimuth of the plane of fire on the ranges is zero.

(2) The influence of the rotation of the earth in our hemisphere causes a deviation of the projectiles to the right of the plane of firing, whatever be its azimuth. This deviation, whose magnitude is independent of the azimuth of the plane of firing, may attain a considerable value. Thus, from Poisson's calculations, a bomb of 32 centims. diameter at 4000 metres would deviate 8 metres in our latitude, owing to the rotation of the earth.

(3) The deviation increases with the latitude; it is greatest at the poles, and zero at the equator.

The influence of the earth's rotation on the aim of the firearms then used was very small relatively to that of the accidental causes which caused considerable variations in the direction and range from

one spot to another. But these variations being now materially reduced in the firing of projectiles by rifled cannon, the influence of the rotation of the earth should be taken into account. This is what I shall show by comparing the deviation due to this motion with the total deviation given by experiment.

As the calculation of the deviation due to the rotation of the earth at any latitude by Poisson's method is very tedious and therefore unpractical, I have used another, which is very expeditious and is virtually as exact as the preceding, as a comparison of the results obtained by each will show.

This method consists simply :—

(1) In calculating the azimuthal angle  $\theta$ , described by the plane of firing about the vertical passing through the mouth of the piece, during the passage of the projectile.

This is performed by M. Foucault's formula,

$$\theta = t \omega \sin \lambda, \dots \dots \dots (1)$$

in which  $\omega$  is the velocity of rotation of the earth about its axis of figure,  $\lambda$  the latitude of the place of experiment, both known quantities.

(2) In multiplying the range given by experiment by  $\sin \theta$ .

So that the deviation  $\Delta$  due to the rotation of the earth is given by the formula

$$\Delta = E \sin \theta = E \sin (t \omega \sin \lambda) * \dots \dots \dots (a)$$

The formulæ of Poisson and this formula give the following results for the firing of mortars of 27 centims. at 1200 metres, and of 32 centims. at 4000 metres, in our latitude :—

	Mortars.	
	of 0 <sup>m</sup> .27.	of 0 <sup>m</sup> .32.
Deviation according to Poisson . . .	1 <sup>m</sup> .20	7 <sup>m</sup> .00
„ „ formula (a) . . .	1 <sup>m</sup> .27	6 <sup>m</sup> .98

The agreement of these results confirms the accuracy of the formula (a).

Applying this latter to the firing of projectiles from rifled cannon, we obtain, for the

FRENCH CANNON.

	Projectiles of				
	4 kil.	2 kil.	12 kil.	50 kil.	80 kil.
$\phi$ , angle of firing . . . . .	17°	14°	45°	45°	50°
E, range . . . . .	3200 <sup>m</sup>	1400 <sup>m</sup>	2800 <sup>m</sup>	3496 <sup>m</sup>	3700 <sup>m</sup>
$t$ , time of flight . . . . .	17 <sup>s</sup>	12 <sup>s</sup>	30 <sup>s</sup>	31 <sup>s</sup>	38 <sup>s</sup>
D, lateral deflection† to the right	198 <sup>m</sup>	46 <sup>m</sup>	310 <sup>m</sup>	494 <sup>m</sup>	870 <sup>m</sup>
$\Delta$ , deviation due to the rotation of the earth . . . . . }	2 <sup>m</sup> .90	1 <sup>m</sup> .67	4 <sup>m</sup> .50	5 <sup>m</sup> .80	7 <sup>m</sup> .10
Ratio $\frac{\Delta}{D}$ . . . . .	$\frac{1}{395}$	$\frac{1}{70}$	$\frac{1}{72}$	$\frac{1}{85}$	$\frac{1}{79}$

\* For latitude 49°, which is virtually that of Paris, we get  $\theta = 10''$ , 98  $t$ .

† The term deflection is applied to the lateral departure of the point at

The smallness of the deviation due to the earth's rotation, as compared with the total deflection, shows that this is practically negligible.

## WHITWORTH'S GUN.

Projectile of 2.75 kil.						
$\phi$ , angle of firing . . . . .	5°	11°	15°	20°	30°	35°
E, range . . . . .	1800m	2800m	4200m	6300m	7200m	9000m
$t$ , time of flight . . . . .	6s.8	13s.6	17s.5	22s.5	33s.0	37s.6
D, total deflection . . . . .	1m.30	3m.14	8m.4	14m.30	22m.30	28m.30
$\Delta$ , deviation due to the earth's rotation . . . . .	0m.63	2m.22	3m.76	6m.35	10m.50	15m.35
Ratio $\frac{\Delta}{D}$ . . . . .	$\frac{1}{2.2}$	$\frac{1}{1.5}$	$\frac{1}{2.0}$	$\frac{1}{2.2}$	$\frac{1}{1.8}$	$\frac{1}{1.8}$

Thus the effect of the earth's rotation contributes half the total deflection of the projectile; hence this influence cannot be neglected.

This deviating effect of the terrestrial rotation may give applications useful in ballistics.

Thus:

(1) When in our hemisphere the effect of the earth's rotation amounts to half the deviation of a projectile to the right of the plane of firing, if the direction of the rifling of the cannon be changed, the deviating action of the air changes also; the effects of rotation and of the resistance of the air destroy each other; so that the projectile will fall in the actual direction of the line of firing, and the deflection will be almost zero.

(2) On passing from one hemisphere to the other, the direction of the rotation changes, and consequently that of the deviating action on the projectile.

It follows that—

If the projectile does not deviate in our hemisphere owing to the equal and contrary effects of the resistance of the air and of the earth's rotation, these effects will be added to one another in the other hemisphere, and the projectile will deviate to the left.

If the deflection to the right in our hemisphere were double that due to the rotation of the earth, as this would change its sign in the opposite hemisphere, the deviating effects of this rotation, and of the resistance of the air, would destroy each other, and there would be no apparent deflection.

Thus the influence of rotation on the deflection of projectiles may become so considerable as to be taken into account, and to receive useful applications in artillery.—*Comptes Rendus*, Sept. 17, 1866.

which the projectile falls from the trace of the plane of firing. Projectiles generally deflect on the same side of the plane. The direction of the deflection depends on that of the screws and of the trace of the projectiles. It is on the right for the guns used in the French army.



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LXVI. *On the Temperature of the Vapours of Boiling Saline Solutions.* By J. GILL, Esq.\*

IN treating of the temperature of the steam evolved from boiling solutions, it should of course be assumed that the steam consists of pure water free from any vestige of the dissolved substance. With this condition, if the steam at atmospheric pressure is observed to be hotter than the boiling-point of pure water under atmospheric pressure, it must evidently be superheated; and in investigating this subject experimentally it is essential to ascertain whether this superheat, if it exist, is imparted to the steam by the hotter boiling liquid itself, and not by conduction or radiation of the walls of the containing vessels. At first sight this condition appears difficult; even in Regnault's apparatus for graduating thermometers, if the boiling liquid were sensibly hotter than pure water boiling under the same pressure, the conduction of heat upwards through the walls of the vessel would communicate some heat to the steam, though probably not of appreciable amount if the formation of steam were comparatively rapid. In the experiments of Professor Magnus† with solutions whose boiling-point was in some cases as high as  $118^{\circ}$ , the conduction of heat upwards through the metal of the apparatus must have been considerable, and could not fail to produce marked effects on the thermometer, both by superheating the steam by contact and radiation, and by radiation on the thermometer itself, if the current of steam were slow.

Gay-Lussac enounced long ago that the temperature of the vapour of any boiling liquid is the same as the temperature of the liquid itself at the spot where the vapour is formed; and Faraday‡

\* Communicated by the Author.

† Poggendorff's *Annalen*, vol. cxii. p. 408.

‡ Quarterly Journal of Science, 1823.

confirmed this opinion, which is no doubt correct for simple liquids in general, and also for solutions as to molecular action in the phenomena; that is to say, each particle of steam is formed in a boiling solution under a tension corresponding to the tension of the vapour of pure water boiling under pressure at the same temperature, the difference between this higher temperature and the common boiling-point of pure water being due to the attraction between the particles of the salt and those of the water. But it would naturally be supposed that, as soon as the newly-formed particles of vapour broke through this sphere of attraction in coalescing to form bubbles, they would at once expand into steam of a tension corresponding to the pressure of the general atmosphere under which they existed, and consequently would form (under atmospheric pressure) common saturated steam at  $100^{\circ}$ , unless they were superheated by the higher temperature of the boiling liquid.

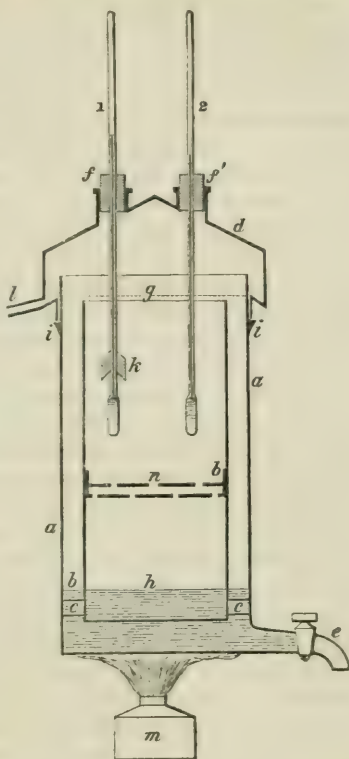
It seems probable that the smallest visible steam-bubble formed in the mass of a boiling liquid should be composed of a vast number of individual vapour particles. It may be imagined that the spherical layer of vapour particles forming the shell of the bubble in contact with the surrounding liquid is at the real temperature of the liquid, and under a tension corresponding to that temperature; but the mass of particles forming the body of the bubble should apparently be at distances from the liquid sufficiently great to place them beyond the attractive influence of the dissolved salt; and if so, this small mass of steam may be supposed, at the instant of its formation, to assume a density and temperature corresponding to the local pressure. If it remained for some time imbedded in the mass of hotter liquid, it might naturally be supposed to become superheated; but the manner in which the communication of heat from the liquid to the vapour might be effected is not perhaps easy to be imagined, nor could the temperature of an individual bubble be practically ascertained. But by surrounding a mass of steam with walls kept constantly wet with a film of the hot solution, it may be placed in circumstances nearly equal to those of a steam-bubble in the body of the liquid, and thus its thermic character may be more conveniently examined. With this view I have used the simple little apparatus shown by the annexed figure; and the results of some experiments I have made with it are, I think, sufficiently remarkable to claim serious attention.

The cylindrical vessel *a* of tin plate, 4 inches in diameter and 7 inches high, has a moveable inner concentric shell *b*, open above and below, held in place by four slight elastic stays *c c*, leaving a free passage of about 1 inch between its lower edge and the bottom of the vessel *a*. The position of the moveable cover *d* is

fixed by the stops *i*; the cover is conical, so that any liquid formed from condensed vapour on its under surface may trickle down into the annular channel which surrounds it, and thence be discharged through the small tube *l*, which also gives exit to the steam. Through the necks *f*, *f'* thermometers fixed in perforated corks may be inserted.

A saturated solution of common salt was prepared which was found to boil at  $109^{\circ}$ . The vessel *a* was filled with this brine to the level of the dotted line *g*, and was caused to boil gently by the spirit-lamp *m*. The neck *f'* being closed with a cork, the thermometer *1* was inserted in the neck *f*. The small conical screen of cork *k* fitting tightly on the stem of the thermometer, prevents moisture from above from trickling down on the bulb, which it also shields in a degree from radiation in that direction. When steam was issuing freely from the small pipe *l*, the thermometer indicated  $109^{\circ}$ . The liquid was now drawn off slowly by the stopcock *e* into a measure previously adjusted, so that the surface of the liquid in *a* would remain approximately at the level *h*, and thus the thermometer was left in an atmosphere of steam with the bulb and the lower part of the stem with its cork screen wet with brine. The double screen *n*, with holes not opposite to each other, shields the thermometer from particles of brine which may be thrown upwards by the boiling liquid. The flame of the lamp was now kept steady, so as to cause a constant current of steam to issue gently from the tube *l*. The surfaces of the shell *b* above the level of the remaining brine would also have been left wet with the same brine. The upper part of the vessel *a* would now be full of steam under atmospheric pressure.

Here we have a thermometer suspended in an atmosphere of



steam supposed to be at  $100^{\circ}$ , according to Rudberg's deductions confirmed by Regnault. According to the experiments of Professor Magnus\*, the temperature of the steam should be about  $106^{\circ}$ . The fact shown by the experiment I am describing is, that the withdrawing of the brine from the thermometer, and the consequent circumstance of its being left in an atmosphere of steam formed and forming from this brine under atmospheric pressure, did not cause any marked effect on its indication of temperature, which remained during some minutes nearly steady at  $109^{\circ}$ . The time could not be greatly prolonged, as the salt thrown down from the evaporating liquid might cause the bottom of the vessel *a* to get injured by the flame; however, the interval was long enough to show that the thermometer indicated very little tendency to lower its temperature; and if the initial circumstances of the experiment could be kept constant, there is every probability that the thermometer would remain steady at the initial temperature of  $109^{\circ}$ , although surrounded by steam at  $100^{\circ}$ . It may also be assumed that the temperature of the shell *b* is the same as that of the thermometer, at the moment when the boiling brine is run off. The sustained temperature of the thermometer must be attributed to the direct thermic action of the steam by contact, or to radiation, or to both these causes together; it is probable, however, that the direct action of the current of steam, even with slow boiling, would greatly exceed that of radiation; and allowing that the steam might, on leaving the liquid, have a temperature of about  $106^{\circ}$  (as found by Magnus) with solutions boiling at  $109^{\circ}$ , the combined effect of this temperature and of radiation from the interior surfaces of the apparatus at  $109^{\circ}$  is still not sufficient to account for the nearly steady temperature of  $109^{\circ}$  shown by the thermometer. The only obvious explanation would be to suppose the steam to be actually superheated to  $109^{\circ}$ . This point was decided as follows:—

As the previous experiment had lasted some minutes, and there was some risk of the bottom of the vessel *a* getting injured from a deposit of salt, the contents were emptied out and the vessel was filled with a fresh portion of the original saturated brine to the upper level *g* as before. After it had been boiling a short time, the thermometer No. 1 indicating  $109^{\circ}$ , the brine was slowly drawn off to the level *h* as before, and during one minute the thermometer was observed to remain steady at  $109^{\circ}$ . The flame of the lamp was kept as nearly as possible steady. It was supposed that thus things were in the same condition as in the previous experiment; and it remained to ascertain (if possible) the real temperature of the mass of steam. A second thermo-

\* *Annales de Chimie*, 3 sér. vol. xii. p. 376, from Poggendorff's *Annalen*.



meter (No. 2) was heated in an air-bath to  $125^{\circ}$ ; and the cork  $f'$  being removed, the thermometer was instantly inserted in its place. The thermometer fell rapidly to  $100^{\circ}\cdot 5$ , and then began to rise slowly; in two minutes it had risen to  $102^{\circ}\cdot 5$ . It was deduced from this, that the real temperature of the steam was most probably  $100^{\circ}$ , and that radiation produced some effect on the dry thermometer, though apparently trifling as compared with the direct thermic action of the steam. The effect of radiation was also noticed on thermometer No. 1, which slowly fell about half a degree, apparently from the proximity of the colder dry thermometer No. 2.

Here we have two thermometers in conditions apparently equal at the moment when the falling temperature of No. 2 had reached the point of  $109^{\circ}$ , or, more correctly, when the temperatures of the two thermometers exactly coincided, excepting that, while No. 2 is dry, No. 1 is supposed to be wet with saturated brine. It must have remained thus wet when the brine in which it was at first immersed was drawn off to the lower level  $h$ ; and being then at a temperature corresponding precisely with the boiling-point of the liquid, surrounded by an atmosphere of saturated steam\* continually forming from the same boiling liquid below, and comparatively isolated from other sources of heat or cold, it could neither evaporate any of its own surrounding film of brine, nor yet condense any of the steam in which it was enveloped. The surfaces of the walls  $b$  would be in the same circumstances, and consequently might be supposed to remain wet with a film of brine at  $109^{\circ}$  as long as the surrounding conditions remained constant. It was seen from the first experiment that the thermometer No. 1 remained at the constant temperature of  $109^{\circ}$  in an atmosphere of steam which the second experiment proved to be at the temperature of about  $100^{\circ}$ . The thermometer No. 2 was carefully observed to have a temperature of  $118^{\circ}$  at the moment it was fixed in the neck  $f'$  of the cover; and it not only fell rapidly to  $109^{\circ}$ , but continued to descend quickly to near  $100^{\circ}$ , the fraction of a degree above this point being evidently due to the heating effects of radiation acting at the same time with the cooling influence of the steam. Here thermometer No. 2 comports itself as the thermometer is supposed universally to do; that is, it equalizes its temperature with that of the medium in which it is immersed; but the first experiment shows clearly that if the thermometer No. 2 were now lowered by sliding its stem through the cork until it dipped into the boiling brine below (the screen  $n$  being supposed to be removed to allow

\* Assumed to be so because ascertained to be of the temperature of  $100^{\circ}$  nearly, under atmospheric pressure.

its passage), it would take the temperature of  $109^{\circ}$ , and retain it after being again drawn up to its original position in the midst of the steam where just before it had shown a temperature of  $100^{\circ}$ . What mysterious virtue can be imagined to exist in the film of brine coating the thermometer which should, through a range of  $9^{\circ}$  in this case, render it insensible to thermic influence supposed to be universal? Does the phenomenon depend merely on the circumstance of the thermometer being coated with a film of some liquid in general? Certainly not; for if the thermometer be heated in an oil-bath instead of an air-bath as described, and inserted in the neck *f'* with the adhering film of oil, it shows very nearly the same as when dry; and no doubt similar results would be obtained with any liquid coating not evaporable in the steam, and between which and the steam no chemical action takes place. It was known long ago that the action of the vapour of water at  $100^{\circ}$  on saline solutions, or on crystals of a salt, may produce temperatures higher than  $100^{\circ}$ ; but it has not been supposed that any substance resulting from the combination of a salt with water should, after the chemical action had ceased, continue to retain its higher temperature during an indefinite time in an atmosphere of steam at  $100^{\circ}$ . M. Rüdorff, a pupil of Magnus, who revived the method of experimenting with a hot thermometer on the vapours of solutions, used by Faraday more than forty years ago, conceived also the idea of first plunging the thermometer into the boiling solution, and after a while raising it into the superincumbent steam; but it appears, from the paper of Magnus above referred to, that he could deduce no certain results from this method. Had he maintained his boiling solutions at a constant degree of saturation, and kept the interior surfaces of his apparatus constantly wet with a film of the hot liquid, he might have been astonished to observe the paradoxical phenomenon of a body considerably hotter than  $100^{\circ}$  remaining in a steam-bath at  $100^{\circ}$  during an indefinite time without lowering its temperature.

If the brine communicated heat to the steam (as we might suppose from the experiments of Magnus), the steam must become superheated in proportion as the brine is cooled; and if the masses of brine and of steam in contact (supposing them isolated from all exterior causes of heating or cooling) were exactly proportioned to their respective thermic influences, it might perhaps be imagined, on a superficial view of the case, that an equalization of temperature might take place between them, the brine becoming colder and consequently tending to condense steam, and the steam becoming superheated and consequently resisting the absorbent action of the brine. But when the film of brine is in permanent contact with an unceasing cur-

rent of steam sweeping over the surface, and continually removing the superheated particles supposed to exist, and replacing them with particles of fresh saturated steam at  $100^{\circ}$ , it is evident that the cooling brine must go on absorbing and condensing more and more steam until in time it would become so diluted as not to differ much from pure water; and, as an inevitable consequence, the temperature must lower in proportion. Now experiment proves that under the conditions mentioned the temperature does not lower; consequently we may conclude that no communication of heat takes place between the brine at  $109^{\circ}$ , and the steam at  $100^{\circ}$ . There seems to be reason to believe that similar results, varying in degree, would be obtained with aqueous solutions of other salts, and with liquids in general when their boiling-point is raised by their holding some substance in solution,—probably also with any amalgam of mercury boiling at a higher temperature than pure mercury. It might also be fairly deduced from analogy, that hot aqueous solutions, though refusing to communicate heat to colder saturated vapour of water, would freely equalize their temperature with a saturated mixture of air and steam at  $100^{\circ}$ , the air alone receiving heat in the process directly from the liquid, and communicating heat to the steam with which it is mixed.

It is not easy in these experiments to maintain the requisite circumstances sufficiently constant to obtain very precise results. In the apparatus described above, the cooling of the vessel *a* from exterior influences causes the film of brine with which its inner surfaces are coated at first to absorb and condense steam. The outer surface of the shell *b* would radiate heat to the colder walls of *a*; and the films of brine with which it is coated on both sides would consequently absorb and condense steam, and so get gradually washed, while the heat conducted upwards through the metal from the boiling brine below would then tend to dry the surfaces and thus superheat the steam. In a variation of the experiment the bottom of *a* was enlarged, and a concentric case was soldered round it, which was kept full of brine maintained at the boiling temperature by the lamp below; but it was perceived that the slight hydrostatic pressure of the column of liquid was sufficient to make the boiling-point of this mass of brine higher than that of the brine boiling at *h*; and hence superheating of the steam would result directly from the drying of the inner surfaces of *a*. If the experiments are made as described in the preceding pages, the first trial generally shows a rapid fall of thermometer No. 2 to near  $100^{\circ}$ . If a little time is allowed to elapse and the experiment is again tried by simply reheating the thermometer, it does not generally show the same fall of temperature the second time. The brine should be removed each



time, the salt cleared out from the bottom, and also from the screen *n* if any should be found there, as sometimes happens, and the vessel filled afresh for the next experiment. For more accurate investigation the film of brine on the surfaces might be continually renewed by mechanical circulation from the mass of boiling liquid below, and the accumulation of salt might be frequently raked off the bottom into a lateral pocket not affected by the lamp, by means of a wire passing through a cork or small stuffing-box or a bit of vulcanized rubber pipe.

Before going further into this curious subject I should wish to see my simple experiments repeated by abler hands, with such amplification as will naturally suggest itself to the intelligent physicist. My own investigation of the subject has been in a manner guided by a train of reasoning which would be out of place here, pointing to results of wide and varied interest; but I imagine that the actual phenomena so far described should interest the experimental philosopher, at least as curiosities of physical science.

Palermo, November 18, 1866.

LXVII. *On the Augmentation of the Disk of the Sun near the Horizon.* By ROBERT TEMPLETON, Esq.

*To the Editors of the Philosophical Magazine and Journal.*

Royal Hibernian Military School, Dublin,  
September 28, 1866.

GENTLEMEN,

THE augmentation of magnitude of the sun and moon at the horizon has in all ages attracted the attention of philosophers, and received various conjectural explanations, two of which, ingenious but eminently unsatisfactory, have survived into the present century; but I am aware of none which have not referred the phenomenon to causes extern to the eye of the observer, to physical rather than psychological agency. On the last day of February, while walking in the church avenue of this Institution, I noticed the sun rising in fiery splendour behind some rather distant trees, and was struck with the distinctness with which the branches of these trees, and with which objects in the horizon right and left, were seen—a peculiar state of the atmosphere, always present on these occasions of augmented disk, favouring this acuteness of vision. It occurred to me at the moment, that my pupil must be dilated to very distant vision; and I observed that the light from the sun was so subdued as to interfere in no way, whether as regarded its own disk or surrounding objects, with this condition of the iris: it also came to my recollection that, at all times when the phenomenon



is observed, the sun and moon are determinately red or reddish orange. It next flashed across my mind that I had somewhere read that Fraunhofer on *one* occasion had remarked, while engaged in examining the spectrum from end to end, that the focal distance of the telescope required to be shortened to a far greater extent than could be accounted for by the refrangibilities. Could then the eye itself be thus singularly affected? It appeared to me there were present two unquestionable facts—a dilated condition of the pupil, and a striking predominance of red rays. Were these conjoined in the production of the phenomenon? It has long been known that certain peculiarities attach to the red ray: it possesses an extraordinary quality for exact definition, it penetrates to vast depths of sea, it can be discerned when no other colour can be seen, and a distinguished physicist informs me that its long-continued use in philosophical investigations produces on the retina an effect bordering on amaurosis. Is it not possible, then, that the eye may be affected in certain states of vision in a way that would prepare us for abnormal results? A consideration of the subject led me first to the remarks contained in *Phil. Mag.* for December, p. 425; but having reached so far, no opportunity occurred for my testing the conjectures which I formed by observing the sun or moon, when augmented, through small holes pierced in a metal plate, until the 24th inst., when the moon favoured me with a trial. As I transferred my eye from hole to hole (beginning with the largest), the diameter became less and less, and the ruddy hue less obvious, till I reached a size (its ordinary size) when the holes diminished it no further, the only effect through the smaller holes being a diminution of brightness from exclusion of more and more rays. Trees and other objects glanced at were unaffected by these holes in their relative distances, being only rendered a little more obscure than when looked at directly. I shortly afterwards examined stars through the holes, and found that they lost their spurious disks and became mere points, remarkably ceasing to twinkle, the residuary effect on the retina appearing to be due to intensity of light as contradistinguished from quantity of light. I am most anxious that these observations should be repeated: in Ireland it is rare to find opportunities, and shall be glad to find in your pages communications confirming or modifying the results I have myself arrived at.

Yours faithfully,

ROBERT TEMPLETON.

P.S. While the proof of the above was in my hands, I tried various combinations of coloured plate glasses, but could not succeed in augmenting the disk to more than double size: the

brightness of the sun was considerably subdued by proximity to the horizon. I suspect the ray I am in search of is but feebly transmitted through glasses so coloured.

Having communicated the substance of the above letter to my friend Professor Stevelly, I received a reply (dated Belfast, November 29, 1866), from which I extract the following:—"I am myself convinced it is the *vera causa*, and I have for more than thirty years taught it as my own conviction, both in my optical and astronomical lectures. What led me to it was exactly your own mode of observing; viz., I made with a needle a fine hole in a piece of sheet-tin lead, laid on a smooth iron, small enough to give me distinct vision of very small print at  $1\frac{1}{2}$  inch distance; this I found brought the setting sun on a very frosty evening to its ordinary apparent size.

"I am also convinced that your opinion as to the cause of the twinkling of the fixed stars is the true one. You mentioned it to me in the year 1828 when we were working together, and I have ever since given it to my class as *yours*."

LXVIII. *On a Method of Calculating the Coefficients of the Lunar Inequalities.* By HENRY HOLT\*.

THE method of undetermined coefficients, the application of which to the calculation of the lunar inequalities was first suggested by D'Alembert (see his *Théorie de la Lune*, p. 107), has been adopted by most writers on the subjects both of the lunar and planetary theories. It is certainly (as D'Alembert himself states) "sans comparaison la plus courte et la plus facile de toutes, puisqu'elle demande ni intégration ni aucune adresse de calcul." It is obvious, however, that, whether the method of undetermined coefficients be employed or not, much of the facility of the computation must depend on the choice of the coordinates and on the selection of the differential equations on which the calculation is to be based. Two different sets of coordinates and equations have been used for this purpose. In one, the coordinates employed are the true values of the moon's longitude, the reciprocal of her curtate radius, and the tangent of her latitude; and the differential equations are functions of these coordinates, the forces *P*, *T*, and *S*, and the time *t*. In the other, the coordinates employed are the mean values of the longitude, radius vector, and latitude; and the differential equations are functions of these mean values, the time *t*, and the disturbance-function *R*. The latter is the method usually adopted in the planetary theory; but it has been applied also to the computation of the lunar in-

\* Communicated by the Author.

equalities, and especially in an elaborate treatise published by Sir J. Lubbock some years since in the Philosophical Transactions. The process of calculation, however, by either method is sufficiently laborious and complicated to render any mode by which the difficulty would be lessened a desideratum. To endeavour in some degree to supply such a mode is the object of the following paper, in which it will be observed the calculation proceeds *directly* from the fundamental equations of motion, thus avoiding the process of integration.

Dublin, October 1866.

1. The three equations of motion referred to polar coordinates are as follow :—

$$\begin{aligned}\frac{d^2\rho}{dt^2} - \rho \frac{dv^2}{dt^2} + P &= 0, \\ 2 \frac{d\rho}{dt} \frac{dv}{dt} + \rho \frac{d^2v}{dt^2} + T &= 0, \\ \frac{d^2}{dt^2} [\rho s] + S &= 0.\end{aligned}$$

For the purposes of calculation the following forms are convenient :—

$$\rho \frac{dv^2}{dt^2} - \frac{d^2\rho}{dt^2} - P = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right] + 2T\rho = 0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{d^2}{dt^2} [\rho s] + S = 0. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

2. In the lunar theory  $-P$ ,  $2T\rho$ , and  $S$  may be thus expressed :

$$\begin{aligned}-P &= -\frac{1}{\rho^2} \left( 1 - \frac{3}{2}s^2 + \frac{15}{8}s^4 \right) + \frac{1}{2}m_l \frac{\rho}{\rho_l^3} + \frac{3}{2}m_l \frac{\rho}{\rho_l^3} \cos 2(v-v_l) \\ &\quad + \frac{9}{8}m_l \frac{\rho^2}{\rho_l^4} \cos (v-v_l) + \frac{15}{8}m_l \frac{\rho^2}{\rho_l^4} \cos 3(v-v_l); \\ 2T\rho &= 3m_l \frac{\rho^2}{\rho_l^3} \sin 2(v-v_l) + \frac{3}{4}m_l \frac{\rho^3}{\rho_l^4} \sin (v-v_l) + \frac{15}{4}m_l \frac{\rho^3}{\rho_l^4} \sin 3(v-v_l); \\ S &= \frac{1}{\rho^2} \left( s - \frac{3}{2}s^3 + \frac{15}{8}s^5 \right) + m_l s \frac{\rho}{\rho_l^3}.\end{aligned}$$

$v$  and  $v_1$  are the true longitudes of the moon and sun measured on the ecliptic supposed fixed.

$\rho$  = moon's true curtate radius, its mean value being unity.

$\rho_1$  = earth's true radius vector.

$s$  = tangent of moon's true latitude.

$m_1$  = mass of sun, the sum of the masses of earth and moon being = 1.

3. The value of  $\rho_1$  is so large in comparison with  $\rho$ , that the terms involving  $\frac{\rho^2}{\rho_1^4}$  and  $\frac{\rho^3}{\rho_1^4}$  may be rejected in the first three approximations, in which case the equations (1), (2), (3) become

$$\rho \frac{dv^2}{dt^2} - \frac{d^2\rho}{dt^2} - \frac{1}{\rho^2} (1 - \frac{3}{2}s^2 + \frac{15}{8}s^4) + \frac{1}{2}m_1 \frac{\rho}{\rho_1^3} + \frac{3}{2}m_1 \frac{\rho}{\rho_1^3} \cos 2(v-v_1) = 0, \quad (4)$$

$$\frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right] + 3m_1 \frac{\rho^2}{\rho_1^3} \sin 2(v-v_1) = 0, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{d^2}{dt^2} [\rho s] + \frac{1}{\rho^2} (s - \frac{3}{2}s^3 + \frac{15}{8}s^5) + m_1 s \frac{\rho}{\rho_1^3} = 0. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

*Planes supposed coincident.*—If the plane of the moon's orbit be supposed to coincide with that of the ecliptic,  $s$  will = 0; hence the equation (6) will disappear, and equations (4), (5) will become

$$\rho \frac{dv^2}{dt^2} - \frac{d^2\rho}{dt^2} - \frac{1}{\rho^2} + \frac{1}{2}m_1 \frac{\rho}{\rho_1^3} + \frac{3}{2}m_1 \frac{\rho}{\rho_1^3} \cos 2(v-v_1) = 0, \quad (7)$$

$$\frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right] + 3m_1 \frac{\rho^2}{\rho_1^3} \sin 2(v-v_1) = 0. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

*Earth's Orbit supposed circular.*—If, in addition to the above hypothesis, we assume that the earth moves in a circular orbit (in other words, if we reject the inequalities of  $v_1$  and  $\frac{1}{\rho_1^3}$  and

suppose  $v_1 = n_1 t + \epsilon_1$ , and  $\frac{1}{\rho_1^3} = \frac{1}{a_1^3}$ , these denoting their mean values respectively), we shall have

$$\rho \frac{dv^2}{dt^2} - \frac{d^2\rho}{dt^2} - \frac{1}{\rho^2} + \frac{1}{2} \frac{m_1}{a_1^3} \rho + \frac{3}{2} \frac{m_1}{a_1^3} \rho \cos 2(v-v_1) = 0, \quad . \quad (9)$$

$$\frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right] + 3 \frac{m_1}{a_1^3} \rho^2 \sin 2(v-v_1) = 0, \quad . \quad . \quad . \quad . \quad (10)$$

$v_1$  in this case denoting the sun's mean longitude  $n_1 t + \epsilon_1$ .

*Rejection of Inequalities of  $v$  and  $\rho$  in the terms  $\frac{3}{2} \frac{m_1}{a_1^3} \rho \cos 2(v-v_1)$*



and  $3\frac{m_1}{a_1^3}\rho^2\sin 2(v-v_1)$ .—Since  $\frac{m_1}{a_1^3}$  is a small fraction ( $=\cdot 0056$  nearly), we may at the outset omit the inequalities of  $v$  and  $\rho$  in the terms  $\frac{3}{2}\frac{m_1}{a_1^3}\rho\cos 2(v-v_1)$  and  $3\frac{m_1}{a_1^3}\rho^2\sin 2(v-v_1)$ , and assume  $v=nt+\epsilon$ ,  $\rho=1$ , these being their mean values. The equations (9) and (10) will thus be reduced to these forms, writing  $k$  for  $\frac{m_1}{a_1^3}$  and  $c_1t^*$  for  $2(nt-nt+\epsilon_1-\epsilon)$ ,

$$\rho\frac{dv^2}{dt^2}-\frac{d^2\rho}{dt^2}-\frac{1}{\rho^2}+\frac{1}{2}k\rho+\frac{3}{2}k\rho\cos c_1t=0, \quad (11)$$

$$\frac{d}{dt}\left[2\rho^2\frac{dv}{dt}\right]+3k\rho\sin c_1t=0. \quad (12)$$

### First approximation.

4. *Variation computed.*—Inspection of these last equations, (11) and (12), shows that the values of  $v$  and  $\rho$  must contain terms involving  $\sin c_1t$  and  $\cos c_1t$ . Let it be required to compute approximately the coefficients of these terms.

*Solution.*—Assume

$$\rho=1+F_1\cos c_1t, \quad v=nt+\epsilon+G_1\sin c_1t,$$

$F_1$  and  $G_1$  being the coefficients whose values are to be determined. It will be convenient to put  $n$  (which represents the moon's mean daily motion in longitude)  $=1$ ,  $t$  denoting the number of days which have elapsed from the epoch. Hence  $c_1$ , which denotes the daily motion of the argument  $2(nt-n_1t+\epsilon-\epsilon_1)$ , will be equal  $2-2n_1$ ,  $n_1$  being the ratio of the sun's mean daily motion in longitude to that of the moon. The values of  $\rho$  and  $v$  will therefore be

$$\rho=1+F_1\cos c_1t, \quad v=t+\epsilon+G_1\sin c_1t.$$

Substituting these values of  $\rho$  and  $v$  in equation (11), rejecting the squares and product of  $F_1$  and  $G_1$ , we shall have

$$\frac{dv}{dt}=1+c_1G_1\cos c_1t, \quad \therefore \frac{dv^2}{dt^2}=1+2c_1G_1\cos c_1t,$$

$$\therefore \rho\frac{dv^2}{dt^2}=1+(F_1+2c_1G_1)\cos c_1t;$$

$$-\frac{d^2\rho}{dt^2}=c_1^2F_1\cos c_1t, \quad -\frac{1}{\rho^2}=-1+2F_1\cos c_1t, \quad \frac{1}{2}k\rho=\frac{1}{2}k+\frac{1}{2}kF_1\cos c_1t.$$

Hence the differential equation (11) becomes

$$0=1+(F_1+2c_1G_1)\cos c_1t+c_1^2F_1\cos c_1t-1+2F_1\cos c_1t+\frac{1}{2}k+\frac{1}{2}kF_1\cos c_1t;$$

\* Or rather  $c_1t+2\epsilon_1-2\epsilon$ ; but the constant part  $2\epsilon_1-2\epsilon$  is omitted, as not affecting the computation of the inequalities.

or collecting the coefficients of  $\cos c_1 t$ , and putting their sum  $= 0$ ,

$$(c_1^2 + \frac{1}{2}k + 3)F_1 + 2c_1G_1 + \frac{3}{2}k = 0. \quad . \quad . \quad (A)$$

Again, substitute the assumed values of  $\rho$  and  $v$  in the equation (12), rejecting, as before, the squares and product of  $F_1$  and  $G_1$ ,

$$\rho^2 = 1 + 2F_1 \cos c_1 t, \quad 2 \frac{dv}{dt} = 2 + 2c_1G_1 \cos c_1 t,$$

$$\therefore 2\rho^2 \frac{dv}{dt} = 2 + (4F_1 + 2c_1G_1) \cos c_1 t,$$

$$\therefore \frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right] = -c_1(4F_1 + 2c_1G_1) \sin c_1 t.$$

Hence equation (12) becomes

$$-c_1(4F_1 + 2c_1G_1) \sin c_1 t + 3k \sin c_1 t = 0,$$

consequently

$$-c_1(4F_1 + 2c_1G_1) + 3k = 0, \text{ or } -4F_1 - 2c_1G_1 = -3 \frac{k}{c_1}.$$

Adding this last equation to the equation (A), we have

$$(c_1^2 + \frac{1}{2}k - 1)F_1 = -3k \left( \frac{1}{2} + \frac{1}{c_1} \right).$$

Also

$$c_1G_1 = \frac{3}{2} \frac{k}{c_1} - 2F_1.$$

If we substitute for  $c_1$  and  $k$  in the above expressions their numerical values as found by observation, viz.

$$c_1 = 2 - 2n_1 = 1.8503974, \quad k = \frac{m_1}{a_1^3} = .005595,$$

we shall find

$$c_1^2 + \frac{1}{2}k - 1 = 2.4267680, \quad F_1 = -.0071962,$$

$$c_1G_1 = .0189279, \quad G_1 = +.0102291.$$

The inequality in longitude is therefore  $.0102291 \sin c_1 t$ , or, reducing to seconds,  $= +2109''.90 \sin c_1 t$ .

The inequality in  $\rho$  is  $= -.0071962 \cos c_1 t$ . If  $P'$  denote the mean parallax ( $57' 4''$ ), the true parallax  $= \frac{P'}{r}$ ; and substituting for  $r$  its approximate value  $1 - .0071962 \cos c_1 t$ , we find the inequality in parallax  $= +24''.62 \cos c_1 t$ .

It may be remarked that the coefficients of the variation as above computed, are much more accurate than those found by the usual methods in the first approximation.

5. *Annual Equation computed.*—In the preceding article, the

calculation being based on equations (11) and (12), the earth's orbit was supposed circular, and  $v_1$  and  $\frac{1}{\rho_1^3}$  were assumed equal to their mean values  $n_1 t + \epsilon_1$  and  $\frac{1}{a_1^3}$ \*. Now both  $v_1$  and  $\frac{1}{\rho_1^3}$  are subject to inequalities, the chief of which depend on the sun's mean anomaly. If these inequalities be taken into account, the values of  $v_1$  and  $\frac{1}{\rho_1^3}$  will be nearly

$$v_1 = n_1 t + \epsilon_1 + (2e_1 - \frac{1}{4} e_1^3) \sin c_2 t, \quad \frac{1}{\rho_1^3} = \frac{1}{a_1^3} [1 + (3e_1 - \frac{9}{8} e_1^3) \cos c_2 t],$$

in which  $c_2 t$  denotes the sun's mean anomaly, and  $e_1$  the eccentricity of the earth's orbit. The effect of these inequalities in the values of  $v_1$  and  $\frac{1}{\rho_1^3}$  will be to introduce into the differential equations, and consequently into the values of  $v$  and  $\rho$ , terms having the sine and cosine of the sun's mean anomaly for arguments. Let it be required to find the coefficients of these terms.

*Solution.*—Assume

$$\rho = 1 + F_2 \cos c_2 t, \quad v = t + \epsilon + G_2 \sin c_2 t,$$

and substitute these values of  $\rho$  and  $v$  in equation (7),

$$\rho \frac{dv^2}{dt^2} = 1 + (F_2 + 2c_2 G_2) \cos c_2 t, \quad -\frac{d^2 \rho}{dt^2} = c_2^2 F_2 \cos c_2 t, \\ -\frac{1}{\rho^2} = -1 + 2F_2 \cos c_2 t,$$

$$\frac{1}{2} m_1 \frac{\rho}{\rho_1^3} = \frac{1}{2} \frac{m_1}{a_1^3} (1 + F_2 \cos c_2 t) (1 + B_2 \cos c_2 t) = \frac{1}{2} k + \frac{1}{2} k (B_2 + F_2) \cos c_2 t,$$

$$\frac{3}{2} m_1 \frac{\rho}{\rho_1^3} \cos 2(v - v_1) = \frac{3}{2} k \cos c_1 t,$$

where

$$B_2 = 3e_1 - \frac{9}{8} e_1^3.$$

Collecting the coefficients of  $\cos c_2 t$  and putting their sum equal to zero, we shall have

$$(c_2^2 + \frac{1}{2} k + 3) F_2 + 2c_2 G_2 + \frac{1}{2} k B_2 = 0. \quad . \quad . \quad (A)$$

\* It may be observed that  $a_1$  is not exactly equal either to the semiaxis major of the earth's orbit, or to the mean value of  $\rho_1$ . If the semiaxis major be denoted by  $a_1$ , the value of  $\frac{1}{a_1^3}$  will be equal to  $\frac{1}{a_1^3} (1 + \frac{3}{2} e_1^2)$  nearly. Hence, though the semiaxis major is a constant quantity, the value of  $\frac{1}{a_1^3}$ , and consequently that of  $k$ , will be affected with a small secular variation chiefly arising from the decrease in the eccentricity  $e_1$ .

Again, substituting the assumed values of  $\rho$  and  $v$  in equation (8),

$$\frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right] = -c_2(4F_2 + 2c_2G_2) \sin c_2t, \quad 3m_1 \frac{\rho^2}{\rho_1^3} \sin 2(v-v_1) = 3k \sin c_2t$$

hence

$$-c_2(4F_2 + 2c_2G_2) = 0, \quad \text{or} \quad -4F_2 - 2c_2G_2 = 0.$$

Adding this last equation to the equation (A), we find

$$(c_2^2 + \frac{1}{2}k - 1)F_2 + \frac{1}{2}kB_2 = 0, \quad \text{or} \quad (c_2^2 + \frac{1}{2}k - 1)F_2 = -\frac{1}{2}kB_2.$$

Also

$$c_2G_2 = -2F_2.$$

If we substitute for  $c_2$  and  $B_2$  their values as found by observation, viz.  $c_2 =$  ratio of motion of sun's anomaly to motion of moon's mean longitude  $= .0748006$ ,  $B_2 = 3e_1 - \frac{9}{8}e_1^3 = .050286$ , we shall have

$$c_2^2 + \frac{1}{2}k - 1 = -.9916174, \quad c_2G_2 = -.00028372, \\ F_2 = +.00014186, \quad G_2 = -.0037930;$$

or, reducing to seconds,

$$\text{Inequality in longitude} = -78''.36 \sin c_2t,$$

$$\text{Inequality in parallax} = -0''.49 \cos c_2t.$$

The coefficient of the annual equation thus found is not so near the true value as that of the variation found in the last article. It will be seen hereafter that the coefficient of  $\sin c_2t$  receives some considerable corrections in the third approximation.

### Second Approximation.

6. We have now calculated the approximate values of the two chief inequalities of the moon's motion (the variation and the annual equation), which are independent of the excentricity of the orbit and its inclination to the ecliptic. If to these two inequalities we add the principal term of the equation depending on the excentricity (which has for its argument the moon's mean anomaly, and the coefficients of which must be found by observation), the values of  $\rho$  and  $v$  will be of these forms,

$$\rho = 1 + F_1 \cos c_1t + F_2 \cos c_2t + F_3 \cos c_3t,$$

$$v = t + \epsilon + G_1 \sin c_1t + G_2 \sin c_2t + G_3 \sin c_3t,$$

$c_3t$  denoting the moon's mean anomaly, and  $F_3, G_3$  being the coefficients of the principal terms in the equation of the moon's centre.

7. If these values of  $\rho$  and  $v$  be substituted in the differential equations (7) and (8), there will arise a series of terms expounding inequalities having for arguments the sum and difference of



each pair of the arguments  $c_1t$ ,  $c_2t$ , and  $c_3t$ , and the coefficients of which will be functions of the products of each pair of the coefficients  $F_1$ ,  $G_1$ ,  $F_2$ ,  $G_2$ ,  $F_3$ ,  $G_3$ , and  $k$ .

Referring to the above values of  $\rho$  and  $v$ , it will be seen that the form of each of the inequalities of  $\rho$  is  $F_l \cos c_l t$ ; and that of the inequalities of  $v$  is  $G_l \sin c_l t$ ; or if we employ the character  $\Sigma$  to signify summation, we may put

$$\rho = 1 + \Sigma F_l \cos c_l t, \quad v = t + \epsilon + \Sigma G_l \sin c_l t.$$

Assume also

$$\frac{1}{\rho_l^3} = \frac{1}{a_l^3} (1 + \Sigma B_l \cos c_l t), \quad 2(v - v_l) = c_l t + \Sigma D_l \sin c_l t.$$

8. Substituting these values in the differential equation (7), omitting the products of three or more inequalities, we shall have

$$(1) \text{ Value of } \rho \frac{dv^2}{dt^2} :$$

$$\frac{dv}{dt} = 1 + \Sigma c_l G_l \cos c_l t,$$

$$\therefore \frac{dv^2}{dt^2} = 1 + 2 \Sigma c_l G_l \cos c_l t + \Sigma \frac{1}{2} c_l G_l c_m G_m \cos (c_l \pm c_m) t;$$

$$\therefore \rho \frac{dv^2}{dt^2} = 1 + \Sigma (F_l + 2c_l G_l) \cos c_l t + \Sigma (c_l G_l F_m + \frac{1}{2} c_l G_l c_m G_m) \cos (c_l \pm c_m) t.$$

$$(2) \text{ Value of } -\frac{d^2 \rho}{dt^2} :$$

$$-\frac{d^2 \rho}{dt^2} = \Sigma c_2^2 F_l \cos c_l t.$$

$$(3) \text{ Value of } -\frac{1}{\rho^2} :$$

$$-\frac{1}{\rho^2} = -1 + \Sigma 2F_l \cos c_l t - \Sigma \frac{3}{2} F_l F_m \cos (c_l \pm c_m) t.$$

$$(4) \text{ Value of } \frac{1}{2} m_l \frac{\rho}{\rho_l^3} :$$

$$\frac{1}{2} \rho = \frac{1}{2} + \frac{1}{2} \Sigma F_l \cos c_l t,$$

$$\frac{m_l}{\rho_l^3} = \frac{m_l}{a_l^3} (1 + \Sigma B_l \cos c_l t) = k + \Sigma k B_l \cos c_l t;$$

$$\therefore \frac{1}{2} m_l \frac{\rho}{\rho_l^3} = \frac{1}{2} k + \Sigma \frac{1}{2} k (F_l + B_l) \cos c_l t.$$

(5) Value of  $\frac{3}{2}m_l \frac{\rho}{\rho_l^3} \cos 2(v-v_l)$  :

$$\frac{3}{2}m_l \frac{\rho}{\rho_l^3} = \frac{3}{2}k + \Sigma \frac{3}{2}k(F_l + B_l) \cos c_l t,$$

$$2(v-v_l) = c_1 t + \Sigma D_l \sin c_l t;$$

$$\therefore \cos 2(v-v_l) = \cos [c_1 t + \Sigma D_l \sin c_l t]$$

(by Taylor's theorem)

$$= \cos c_1 t - \sin c_1 t \cdot \Sigma D_l \sin c_l t$$

$$= \cos c_1 t + \Sigma \frac{1}{2} D_l \cos (c_1 + c_l) t - \Sigma \frac{1}{2} D_l \cos (c_1 - c_l) t;$$

$$\therefore \frac{3}{2}m_l \frac{\rho}{\rho_l^3} \cos 2(v-v_l) = \frac{3}{2}k \cos c_1 t + \Sigma \frac{3}{4}k(B_l + F_l + D_l) \cos (c_1 + c_l) t \\ + \Sigma \frac{3}{4}k(B_l + F_l - D_l) \cos (c_1 - c_l) t.$$

Hence, collecting these values, equation (7) becomes

$$0 = \Sigma [(c_l^2 + \frac{1}{2}k + 3)F_l + 2c_l G_l] \cos c_l t + \Sigma \frac{1}{2}k B_l \cos c_l t, \\ + \frac{3}{2}k \cos c_1 t \\ + \Sigma \frac{3}{4}k(B_l + F_l + D_l) \cos (c_1 + c_l) t \\ + \Sigma \frac{3}{4}k(B_l + F_l - D_l) \cos (c_1 - c_l) t \\ + \Sigma (c_l G_l F_m - \frac{3}{2}F_l F_m + \frac{1}{2}c_l G_l c_m G_m) \cos (c_l \pm c_m) t.$$

Applying this equation to the case of any given argument  $c_x t$ , we shall have

$$0 = (c_x^2 + \frac{1}{2}k + 3)F_x + 2c_x G_x + \frac{1}{2}k B_x \\ + \frac{3}{2}k \text{ in the case when } x=1, \\ + \frac{3}{4}k(B_l + F_l + D_l) \text{ when } c_x = c_1 + c_l, \\ + \frac{3}{4}k(B_l + F_l - D_l) \text{ when } c_x = c_1 - c_l, \\ + \Sigma (c_l G_l F_m - \frac{3}{2}F_l F_m + \frac{1}{2}c_l G_l c_m G_m) \text{ when } c_x = c_l \pm c_m \dots (A)$$

9. Again, substitute the assumed values of  $\rho$  and  $v$  in the differential equation (8).

(1) Value of  $\frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right]$  :

$$\rho^2 = 1 + \Sigma 2F_l \cos c_l t + \Sigma \frac{1}{2} F_l F_m \cos (c_l \pm c_m) t,$$

$$2 \frac{dv}{dt} = 2 + \Sigma 2c_l G_l \cos c_l t;$$

$$\begin{aligned}\therefore 2\rho^2 \frac{dv}{dt} &= 2 + \Sigma (4F_l + 2c_l G_l) \cos c_l t \\ &\quad + \Sigma (F_l F_m + 2c_l G_l F_m) \cos (c_l \pm c_m) t; \\ \therefore \frac{d}{dt} \left[ 2\rho^2 \frac{dv}{dt} \right] &= -\Sigma c_l (4F_l + 2c_l G_l) \sin c_l t \\ &\quad - \Sigma (c_l \pm c_m) (F_l F_m + 2c_l G_l F_m) \sin (c_l \pm c_m) t.\end{aligned}$$

(2) Value of  $3m_l \frac{\rho^2}{\rho_l^3} \sin 2(v - v_l)$ :

$$3 \frac{m_l}{\rho_l^3} = 3k + \Sigma 3k B_l \cos c_l t,$$

$$\rho^2 = 1 + \Sigma 2F_l \cos c_l t,$$

$$\sin 2(v - v_l) = \sin (c_l t + \Sigma D_l \sin c_l t)$$

(by Taylor's theorem)

$$= \sin c_l t + \cos c_l t \cdot \Sigma D_l \sin c_l t$$

$$= \sin c_l t + \Sigma \frac{1}{2} D_l \sin (c_l + c_l) t - \Sigma \frac{1}{2} D_l \sin (c_l - c_l) t;$$

$$\begin{aligned}\therefore 3m_l \frac{\rho^2}{\rho_l^3} \sin 2(v - v_l) &= 3k \sin c_l t + \Sigma \frac{3}{2} k (B_l + 2F_l + D_l) \sin (c_l + c_l) t \\ &\quad + \Sigma \frac{3}{2} k (B_l + 2F_l - D_l) \sin (c_l - c_l) t.\end{aligned}$$

Consequently, collecting these values, equation (8) becomes

$$\begin{aligned}0 &= 3k \sin c_l t \\ &\quad - \Sigma c_l (4F_l + 2c_l G_l) \sin c_l t \\ &\quad + \Sigma \frac{3}{2} k (B_l + 2F_l + D_l) \sin (c_l + c_l) t \\ &\quad + \Sigma \frac{3}{2} k (B_l + 2F_l - D_l) \sin (c_l - c_l) t \\ &\quad - \Sigma (c_l \pm c_m) (F_l F_m + 2c_l G_l F_m) \sin (c_l \pm c_m) t;\end{aligned}$$

and applying this equation to the case of a given argument  $c_x t$ , we shall have

$$0 = 3k \text{ in the case when } x = 1,$$

$$\begin{aligned}&-c_x (4F_x + 2c_x G_x) \\ &+ \frac{3}{2} k (B_l + 2F_l + D_l) \text{ when } c_l + c_l = c_x, \\ &+ \frac{3}{2} k (B_l + 2F_l - D_l) \text{ when } c_l - c_l = c_x, \\ &- \Sigma c_x (F_l F_m + 2c_l G_l F_m) \text{ when } c_l \pm c_m = c_x.\end{aligned}$$

Dividing each of these terms by  $c_x$ ,

$$\begin{aligned}
 0 &= 3 \frac{k}{c_1} \text{ in the case when } x=1, \\
 &\quad - (4F_x + 2c_x G_x) \\
 &\quad + \frac{3}{2} \frac{k}{c_x} (B_l + 2F_l + D_l) \text{ when } c_x = c_1 + c_l, \\
 &\quad + \frac{3}{2} \frac{k}{c_x} (B_l + 2F_l - D_l) \text{ when } c_x = c_1 - c_l, \\
 &\quad - \Sigma (F_l F_m + 2c_l G_l F_m) \text{ when } c_x = c_l \pm c_m. \quad \dots \quad (B)
 \end{aligned}$$

Adding this last equation to the equation (A), article 8, we find, denoting  $B_l + 2F_l + D_l$  by  $M_l$ , and  $B_l + 2F_l - D_l$  by  $N_l$ ,

$$\begin{aligned}
 (c_x^2 + \frac{1}{2}k - 1)F_x &= -\frac{1}{2}kB_x \\
 &\quad - 3k \left( \frac{1}{2} + \frac{1}{c_1} \right) \text{ in the case where } x=1, \\
 &\quad - \frac{3}{2}k \left[ \frac{1}{2}(M_l - F_l) + \frac{1}{c_x} M_l \right] \text{ where } c_1 + c_l = c_x, \\
 &\quad - \frac{3}{2}k \left[ \frac{1}{2}(N_l - F_l) + \frac{1}{c_x} N_l \right] \text{ where } c_1 - c_l = c_x, \\
 &\quad + \Sigma \left[ \left( \frac{5}{2}F_l + c_l G_l \right) F_m - \frac{1}{2}c_l G_l c_m G_m \right] \text{ where } c_l \pm c_m = c_x. \\
 c_x G_x &= \frac{3}{2} \frac{k}{c_1} \text{ in the case where } x=1, \\
 &\quad - 2F_x \\
 &\quad + \frac{3}{4} \frac{k}{c_x} M_l \text{ where } c_1 + c_l = c_x, \\
 &\quad + \frac{3}{4} \frac{k}{c_x} N_l \text{ where } c_1 - c_l = c_x, \\
 &\quad - \Sigma \left( \frac{1}{2}F_l + c_l G_l \right) F_m \text{ where } c_l \pm c_m = c_x.
 \end{aligned}$$

11. Hence we have the following *Rules for calculating the Inequalities of the second order*:—

(1) Any inequality  $B_l \cos c_l t$  in the value of  $\frac{a_l^3}{\rho_l^3}$  produces the following:

$$\left. \begin{aligned}
 &\text{Inequality in } \rho = F_l \cos c_l t, \text{ where } F_l = -\frac{1}{2} \frac{k}{h} \cdot B_l \\
 &\text{Inequality in } v = -\frac{2}{c} F_l \sin c_l t, \text{ where } h_l = c_l^2 + \frac{1}{2}k - 1.
 \end{aligned} \right\} (A)$$



(2) If  $c_l t$  denote any argument, and if  $F_l$ ,  $B_l$ , and  $D_l$  denote the coefficients of the corresponding inequalities in  $\rho$ ,  $\frac{a_l^3}{\rho_l^3}$ , and  $2(v-v_l)$  respectively, then there will arise the following :

$$\left. \begin{array}{l} \text{Inequalities} \\ \text{in } \rho \end{array} \right\} \left\{ \begin{array}{l} F_x = -\frac{3}{2} \frac{k}{h_x} \left[ \frac{1}{2} (M_l - F_l) + \frac{1}{c_x} M_l \right] \cos c_x t, \\ F_y = -\frac{3}{2} \frac{k}{h_y} \left[ \frac{1}{2} (N_l - F_l) + \frac{1}{c_y} N_l \right] \cos c_y t, \end{array} \right. \\ \left. \begin{array}{l} \text{Inequalities} \\ \text{in } v \end{array} \right\} \left\{ \begin{array}{l} G_x = \frac{1}{c_x} \left( \frac{3}{4} \frac{k}{c_x} M_l - 2F_x \right) \sin c_x t, \\ G_y = \frac{1}{c_y} \left( \frac{3}{4} \frac{k}{c_y} N_l - 2F_y \right) \sin c_y t, \end{array} \right. \quad (B)$$

where

$$c_x = c_1 + c_l, \quad c_y = c_1 - c_l, \quad h_x = c_x^2 + \frac{1}{2}k - 1, \quad h_y = c_y^2 + \frac{1}{2}k - 1, \\ M_l = B_l + 2F_l + D_l, \quad N_l = B_l + 2F_l - D_l.$$

(3) If  $c_l t$  and  $c_m t$  denote any pair of arguments, and if  $F_l$ ,  $F_m$ ,  $G_l$ ,  $G_m$  denote the coefficients of the corresponding inequalities in  $\rho$  and  $v$ , then there will arise the following :

$$\left. \begin{array}{l} \text{Inequalities in } \rho: F_x = \frac{1}{h_x} \left[ \left( \frac{5}{2} F_l + c_l G_l \right) F_m - \frac{1}{2} c_l G_l c_m G_m \right] \cos c_x t, \\ \text{Inequalities in } v: G_x = -\frac{1}{c_x} \left[ \left( \frac{1}{2} F_l + c_l G_l \right) F_m + 2F_x \right] \sin c_x t, \end{array} \right\} \quad (C)$$

where

$$c_x = c_l \pm c_m, \quad h_x = c_x^2 + \frac{1}{2}k - 1.$$

11. With the aid of these formulæ the inequalities of the second order can be calculated with great facility. For this purpose it is only necessary to put  $l$  and  $m=1, 2$ , and  $3$  successively, and to substitute for  $F_l$ ,  $G_l$ , &c. their values, either those already computed, or as determined by observation, viz. :—

$$\begin{array}{lll} c_1 = +1.8503974, & c_2 = .0748006, & c_3 = .991548, \\ c_1 G_1 = .0189279, & c_2 G_2 = -.00028372, & c_3 G_3 = .1088310, \\ B_1 = 0, & B_2 = .050286, & B_3 = 0, \\ F_1 = -.0071962, & F_2 = +.0001419, & F_3 = -.054696, \\ D_1 = .0204762, & D_2 = -.059468, & D_3 = +.2195174. \end{array}$$

12. Substituting these values in the formulæ (B) of Art. 10, we find the following :—

	Inequalities of $\rho$ .	Inequalities of $v$ .
When $l=1$	$-.00000547 \cos 2c_1 t$	$+.00000482 \sin 2c_1 t$
$l=2$	$\begin{cases} +.00002832 & (c_1+c_2)t \\ -.00045522 & (c_1-c_2)t \end{cases}$	$\begin{cases} -.00003950 & (c_1+c_2)t \\ +.00065920 & (c_1-c_2)t \end{cases}$
$l=3$	$\begin{cases} -.00014364 & (c_1+c_3)t \\ -.01681440 & (c_1-c_3)t \end{cases}$	$\begin{cases} +.00015830 & (c_1+c_3)t \\ +.03728454 & (c_1-c_3)t \end{cases}$

Again, substituting in the formulæ (C), we find

When $l=1$ & $m=1$	$-.00001464 \cos 2c_1 t$	$+.00003771 \sin 2c_1 t$
$l=1$ & $m=2$	$\begin{cases} +.00000104 & (c_1+c_2)t \\ +.00000131 & (c_1-c_2)t \end{cases}$	$\begin{cases} -.00000221 & (c_1+c_2)t \\ -.00000270 & (c_1-c_2)t \end{cases}$
$l=1$ & $m=3$	$\begin{cases} -.00015273 & (c_1+c_3)t \\ +.00416537 & (c_1-c_3)t \end{cases}$	$\begin{cases} +.00040253 & (c_1+c_3)t \\ -.00872359 & (c_1-c_3)t \end{cases}$
$l=2$ & $m=1$	$\begin{cases} +.00000080 & (c_2+c_1)t \\ +.00000101 & (c_2-c_1)t \end{cases}$	$\begin{cases} -.00000163 & (c_2+c_1)t \\ +.00000200 & (c_2-c_1)t \end{cases}$
$l=2$ & $m=2$	$+.00000003 \quad 2c_2 t$	$-.00000020 \quad 2c_2 t$
$l=2$ & $m=3$	$\begin{cases} +.00008269 & (c_2+c_3)t \\ -.00007368 & (c_2-c_3)t \end{cases}$	$\begin{cases} -.00016601 & (c_2+c_3)t \\ -.00014805 & (c_2-c_3)t \end{cases}$
$l=3$ & $m=1$	$\begin{cases} -.00011712 & (c_3+c_1)t \\ +.00031341 & (c_3-c_1)t \end{cases}$	$\begin{cases} +.00028875 & (c_3+c_1)t \\ +.00675538 & (c_3-c_1)t \end{cases}$
$l=3$ & $m=2$	$\begin{cases} +.00008212 & (c_3+c_2)t \\ -.00007317 & (c_3-c_2)t \end{cases}$	$\begin{cases} -.00016486 & (c_3+c_2)t \\ +.00014702 & (c_3-c_2)t \end{cases}$
$l=3$ & $m=3$	$-.00149753 \quad 2c_3 t$	$+.00375768 \quad 2c_3 t$

Lastly, the value of  $\frac{a_l^3}{\rho_l^3}$  contains one inequality of the second order, viz.  $+\frac{3}{2}e_l^2 \cos 2c_2 t$ ; or substituting for  $e_l$  its value  $.016764$ , we have  $\frac{3}{2}e_l^2 = +.001264$ . Substituting this in the formulæ (A), we find

Inequality in  $\rho = +.00000363 \cos 2c_2 t$ ,

Inequality in  $v = -.00004853 \sin 2c_2 t$ .

13. Collecting, therefore, the coefficients of like arguments, remembering that  $\cos(-x) = \cos x$  and  $\sin(-x) = -\sin x$ , we obtain finally the following

*Inequalities of the Second Order.*

Argument.	Value of argument according to common notation.	Inequalities of $\rho$ .	Inequalities of $v$ .	
			In parts radii.	In seconds.
$(c_1 - c_3)t$	$2(\odot - \ominus) - A$	$-.00945432$	$+.02180557 =$	$+4497.72^*$
$2c_1 t$	$2A$	$-.00149753$	$+.00375768 =$	$+775.08^\dagger$
$(c_1 + c_3)t$	$2(\odot + \ominus) + A$	$+.00041349$	$+.00084958 =$	$+175.24$
$(c_1 - c_2)t$	$2(\odot - \ominus) - A'$	$-.00045290$	$+.00065450 =$	$+135.00$
$2c_1 t$	$2A$	$+.00000366$	$-.00004873 =$	$-10.05$
$2c_2 t$	$4(\odot - \ominus)$	$-.00002011$	$+.00004253 =$	$+8.77$
$(c_1 + c_2)t$	$2(\odot + \ominus) + A'$	$+.00005016$	$-.00004334 =$	$-8.94$
$(c_1 + c_2)t$	$A + A'$	$+.00016481$	$-.00033087 =$	$-68.25$
$(c_1 - c_2)t$	$A - A'$	$-.00014685$	$+.00029507 =$	$+60.86$

\* Evection.

† Second term of equation of the centre.

Four of the above coefficients differ considerably from their values found by observation: it will be found that they receive corrections when the approximation is extended to terms of the fourth order.

The facility of the method of computation above given can be appreciated only by those who have actually gone through the investigation according to the usual methods. I purpose, in a future paper, to carry the approximation as far as terms of the third and fourth order, and to remark on one or two points connected with the method which require elucidation.

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LXIX. *On the Absorption and Dialytic Separation of Gases by Colloid Septa.* By THOMAS GRAHAM, F.R.S., Master of the Mint.

[Continued from p. 420.]

PART II.—*Action of Metallic Septa at a red heat.*

*Platinum.*

THE surprising passage of gases through the homogeneous substance of a plate of fused platinum or of iron at a red heat, lately discovered by MM. H. St.-Claire Deville and Troost, may possibly prove to be analogous in its mode of occurrence to the passage of gases through the rubber septum. At the same time it must be admitted that such an hypothesis as that of liquefaction can only be applied in a general and somewhat vague manner to bodies so elastic and volatile at an elevated temperature as the gases generally must be, and hydrogen in particular. Still some degree of absorbing and liquefying power can scarcely be denied to a soft or liquid substance, in whatever circumstances it may be found, with such a patent fact before us as the retention by fused silver of 18 or 20 volumes of oxygen at a red heat. It may safely be assumed that the tendency of gases to liquefaction, however much abated by temperature, is too essential a property of matter to be ever entirely obliterated.

A little consideration also shows that the absorption of gas by a liquid or by a colloid substance is not a purely physical effect. The absorption appears to require some relation in composition—as where both the gas and the liquid are hydrocarbons, and the affinity or attraction of solution can come into play. May a similar analogy be looked for of hydrogen to liquid or colloid bodies of the metallic class?

With reference to the mechanical pores of a solid mass, liquids are probably more penetrating than gases. The former show often a power of adhesion to solids, while gases appear to be es-

entially repulsive. A degree of minute porosity is conceivable, which will admit a liquid, but may be impassable to a gas, even under its molecular movement of diffusion.

Finally, there is presented to us a bold and original conjecture by M. Deville, in explanation of his own observations. It is clearly expressed in the following quotation taken from the last publication of M. Deville on this subject:—

“La perméabilité de la matière est d’une nature toute différente dans les corps homogènes, comme le fer et le platine, et dans des pâtes plus ou moins discontinues, resserrées par la cuisson ou la pression, comme la terre à creuset, la plombagine, dont M. Graham s’est servi dans ses mémorables expériences. Dans les métaux, la porosité résulte de la dilatation que la chaleur fait éprouver aux espaces intermoléculaires; elle est en relation avec la forme des molécules que l’on peut toujours supposer régulières, et avec leur alignement qui détermine le clivage ou les plans de facile fracture des masses cristallisées. C’est cet intervalle intermoléculaire que le phénomène de la porosité des métaux purs et fondus accuse avec une évidence éclatante, c’est aussi par ce phénomène qu’on peut espérer de calculer la distance des molécules solides aux températures élevées où les gaz peuvent s’y introduire.”

A new kind of porosity in metals is imagined, of a greater degree of minuteness than the porosity of graphite and earthenware. This is an intermolecular porosity due entirely to dilatation. The intermolecular porosity of platinum and iron is not sufficient to admit any passage of gas at low temperatures, but is supposed by M. Deville to be developed by the expansive agency of heat upon the metals, and to become sensible at the temperature of ignition. Such a species of porosity, if it exists, may well be expected to throw light on the distances of solid molecules at elevated temperatures, when gases introduce themselves. The ready passage through platinum of some gases, particularly of hydrogen, and the difficult passage of others render such molecular views the more remarkable.

The passage of hydrogen through the substance of heated platinum appears in its most simple aspect when the gas is allowed to make its way through the metal into a vacuous space. The experiment of M. Deville, where a tube of platinum charged with nitrogen is placed within a large porcelain tube charged with hydrogen\*, was modified by placing the platinum tube, closed at one end, in communication by the other (open) extremity with the Sprengel pump, so that a vacuum was substituted for the nitrogen. It was then easy to observe that a vacuum in the platinum tube was preserved for hours when the external

\* *Comptes Rendus*, vol. lvii. p. 965.



gas admitted into the annular space between the porcelain and platinum tubes was either atmospheric air or hydrogen at the natural temperature. The tubes being placed across an empty furnace, the latter was now lighted; and it was seen that, with air circulating outside the platinum, the vacuum remained undisturbed, even when the temperature of the tubes rose to a bright red heat. But when dry hydrogen was driven through the same annular space, the platinum, while continuing impermeable at all temperatures below a dull red heat, began to admit hydrogen to the vacuum as soon as the external porcelain tube became visibly red-hot. In seven minutes the Sprengel pump now delivered 15·47 cub. centims. of gas, of which 15·27 cub. centims. appeared, by explosion with oxygen, to be hydrogen.

In a repetition of the last experiment, hydrogen dried by sulphuric acid was again allowed to circulate in excess outside the platinum. After a vacuum was once obtained within the platinum tube, the gas delivered by the Sprengel pump, in the cold, during a period of forty minutes, amounted to no more than a bubble of the size of a pin-head, showing the tightness of the apparatus. The Sprengel pump being constantly kept in action, the tubes were now heated to redness, and then gradually to a temperature approaching a white heat. The gas delivered each five minutes was found to be 13, 15·5, 17·4, 16·9, 18·6 cub. centims. as the temperature rose. These volumes are referred to a temperature of 20° and barometer of 760 millims. The last observation gives a passage of 3·72 cub. centims. of hydrogen per minute. The platinum tube employed here was joined without solder, having been drawn from a mass of platinum which had been aggregated by fusion. It was similar in this respect to the tube employed by M. Deville. The tube was 0·812 metre in length (32 inches) and 1·1 millim. in thickness, with an internal diameter of 12 millims. But only a portion of about 200 millims. (8 inches) of the tube was heated to redness in the furnace experiment. The inner surface of the heated portion had therefore an area of 0·0076 square metre. Hence one square metre of heated platinum delivered 489·2 cub. centims. of hydrogen per minute. This result admits of comparison with the passage of gases through a septum of rubber. In the most favourable circumstances, when the thin membrane of a rubber balloon was employed, the passage of air into a vacuum was at the rate of 26·5 cub. centims. per square metre in one minute. The passage of hydrogen may be taken as 4·8 times as rapid as that of atmospheric air, or at 127·2 cub. centims. per minute. But while the thickness of the platinum septum was 1·1 millim., that of the rubber film was only one-seventieth part of a millimetre. Hence we have the ultimate comparison:—

Passage of hydrogen gas in one minute through a septum of 1 square metre,—

Through rubber 0.014 millim. in thickness, 127.2 cub. centims. at 20° C.;

Through platinum 1.1 millim. in thickness, 489.2 cub. centims. at bright red heat.

If the permeation of hydrogen is due to the same agency in both septa, can the vast superiority of the platinum septum be connected with its greatly higher temperature?

It was interesting now to turn from hydrogen to the passage of other gases through heated platinum. The experiments were all made in the same way, and at a full red heat. The temperature, it will be observed, was short of that at which the elements of water and carbonic acid are partially dissociated.

*Oxygen and Nitrogen.*—Atmospheric air, which may be taken to represent both of these gases, was now allowed to flow through the annular space between the tubes, the interior platinum tube being kept vacuum as usual. In one hour the gas collected by the constant action of a Sprengel pump amounted only to 0.3 cub. centim. Hydrogen in the same time would have given 211 cub. centims. It is very doubtful, too, whether the trifling fraction of a centimetre of gas collected had all passed through the platinum; a part (or the whole of it) may have entered by the joints of the apparatus. Platinum, then, cannot be said to be sensibly permeable to either oxygen or nitrogen, even at a full red heat.

*Carbonic acid.*—This gas was supplied from a bottle containing marble, by the action of pure hydrochloric acid, the gas being afterwards washed with water and dried by sulphuric acid in its way to the exterior porcelain tube. In one hour the interior platinum tube yielded only three-tenths of a cubic centimetre of gas, of which, again, only an indeterminate small portion was condensed by baryta-water and appeared to be carbonic acid. The passage of carbonic acid is therefore incalculably small at a full red heat.

*Chlorine.*—This gas, evolved slowly from a glass flask containing peroxide of manganese and hydrochloric acid, was washed by water, dried by sulphuric acid, and thrown as usual into the porcelain tube so as to occupy the annular space between the two tubes. A small tube containing slaked lime was interposed between the end of the platinum tube and the Sprengel pump, so as to absorb the chlorine, if any came through the substance of the platinum. After the tube had been heated for an hour, the lime was examined for chlorine, but did not contain a trace of that substance. A minute quantity of gas, probably air, amounting to 0.15 cub. centim., was collected during the time. Plati-

num, then, is not sensibly penetrated by chlorine at a red heat.

*Hydrochloric acid*, dried over sulphuric acid, was passed for one hour through the porcelain tube. About 0.5 cub. centim. of gas was collected from the platinum tube, which contained no hydrochloric acid and no free hydrogen. The ignited platinum, then, is not penetrated by hydrochloric acid; nor does it appear to dissociate the elements of that gas at the temperature of the experiment.

*Vapour of water*.—A stream of steam was carried for one hour through the porcelain tube. During that time half a cub. centim. of gas appeared to be drawn from the platinum tube, which gas contained no hydrogen. There is no evidence of the passage through the platinum of the vapour of water, nor of its decomposition.

*Ammonia*.—This gas appeared to be decomposed to a considerable extent in passing through the heated annular space, hydrogen passing freely at the same time through the ignited platinum. No trace of undecomposed ammonia, although the gas was transmitted in considerable excess, was discovered accompanying the free hydrogen found in the platinum tube. When the ammonia was evolved slowly, the quantity of hydrogen entering the platinum tube amounted to 16.4 cub. centims. in five minutes, or was sensibly the same as when pure hydrogen was carried through the annular space. Ammonia, then, appears to be incapable of penetrating the ignited platinum.

*Coal-gas*.—When coal-gas was carried through the porcelain tube, the following quantities of hydrogen came through the platinum in successive periods of twenty minutes each—13.3 cub. centims., 5.2, and 8.8. The first portion, when exploded with oxygen, did not disturb baryta-water after condensation; 13.3 cub. centims. contained 13.16 cub. centims. of hydrogen. It appears, then, that the permeating gas was free hydrogen only, and that no compound of carbon present in coal-gas was capable of passing through the platinum. This may be held as excluding the passage of *carbonic oxide*, *marsh-gas*, and *olefiant gas*, all represented in the coal-gas.

*Hydrosulphuric acid*.—This gas, prepared from sulphide of antimony and hydrochloric acid, washed, and dried over chloride of calcium, was then circulated through the outer porcelain tube. The hydrosulphuric acid was nearly all decomposed into sulphur and hydrogen, the latter coming through the platinum at the rate of 9 cub. centims. in five minutes. A trace of hydrosulphuric acid may also have passed through, as the mercury of Sprengel's tube was slightly soiled; but no indication of this gas could be perceived in the hydrogen collected. It appears,

then, that hydrosulphuric acid is to be classed among the non-penetrating gases. The result appears to be:—

I. Gas capable of passing through a septum of platinum 1·1 millim. in thickness at a full red heat.

Hydrogen (211 cub. centims. per hour).

II. Gases incapable of passing through a septum of fused platinum 1·1 millim. in thickness at a full red heat.

Oxygen . . .	(not to the extent of 0·2 cub. centim. per hour.)		
Nitrogen . . .	”	”	”
Chlorine . . .	”	”	”
Hydrochloric acid	”	”	”
Vapour of water .	”	”	”
Carbonic acid .	”	”	”
Carbonic oxide .	”	”	”
Marsh-gas ( $\text{C H}_4$ )	”	”	”
Olefiant gas . .	”	”	”
Hydrosulphuric acid	”	”	”
Ammonia . . .	”	”	”

It remains to be discovered whether a sensible passage of any of these gases could be effected through a platinum septum much reduced in thickness, or through the same septum under the influence of a considerably higher temperature. A fallacious appearance of permeation is sometimes occasioned by the escape from the platinum itself of a small quantity of gas, particularly of carbonic oxide and hydrogen, as will immediately appear. The permeation is in consequence never unequivocal for the first hour or two that the platinum septum is heated.

One of the curious experiments of M. Deville was repeated, in which hydrogen appears to escape from the platinum tube pretty much as the same gas would escape from a graphite diffusimeter—the platinum tube being full of hydrogen, while the annular space between the platinum and outer porcelain tube was occupied by atmospheric air. At the maximum temperature the supply of hydrogen to the platinum tube was shut off, as that gas entered at one end of the tube, while the other end of the platinum tube was left in connexion with a barometer-tube dipping into a cistern of mercury. Immediately the mercury began to rise in the gauge tube from the passage of hydrogen outwards through the walls of the platinum tube; and the latter in the end became nearly vacuous from the complete escape of the hydrogen.



Heated platinum tube containing hydrogen ; air outside.

Time.	Rise of mercury in gauge barometer.
0 minute.	0 millim.
10 minutes.	115 millims.
20    "	245    "
30    "	400    "
40    "	535    "
50    "	645    "
60    "	710    "

the actual height of the atmospheric barometer being 750 mil-  
lims. at the same time. The tension of the residual gas was  
therefore no more than 40 millims. of mercury. The ratio be-  
tween the volume of gas at the beginning and end of the hour is  
here as 18·75 to 1 ; whereas in a diffusion experiment of hydro-  
gen into air, the ratio would be as 3·8 to 1. Further, the resi-  
dual gas in the platinum tube still retained a small portion of  
hydrogen. Withdrawn by means of the Sprengel pump and ex-  
amined, the residual gas in the platinum tube amounted to 3·56  
cub. centims., and consisted of

Nitrogen . . .	3·22 cub. centims.
Hydrogen . . .	0·34 cub. centim.
	3·56 cub. centims.

The available capacity of the platinum tube was 113·1 cub.  
centims. ; and when the tube was heated, the gas driven out by  
dilatation measured in the cold 39·5 cub. centims., leaving in the  
hot platinum tube 73·6 cub. centims. of gas estimated at 20° C.  
and barom. 760 millims. It was found necessary in these expe-  
riments to stuff that portion of the platinum tube that was placed  
across the furnace and strongly heated, with asbestos, to give  
support to the tube when softened by the heat of ignition, and  
to prevent the tube from collapsing.

It is difficult to say where the small volume of nitrogen found  
in the platinum tube, amounting to 3·22 cub. centims., actually  
came from. It appears too great in amount to have formed an  
impurity in the original hydrogen gas, or to have gained access  
to the vacuum through defective joinings in the apparatus. Its  
presence suggests the inquiry, admitting that nitrogen cannot  
pass alone through platinum into a vacuum, whether the same  
gas may not be enabled to pass, in some small proportion, while  
hydrogen is simultaneously travelling through the platinum in  
the opposite direction. The liquid or the gaseous hydrogen oc-  
cupying the platinum septum would thus form a vehicle or chan-

nel, by the help of which another analogous body like nitrogen might be conceived capable of passing through the platinum in small quantity, by a process of liquid or gaseous diffusion.

*Absorption and detention of Hydrogen by Platinum.*—The passage of a gas through a colloid septum is preceded by the condensation of the gas in the substance of the septum, according to the views taken in this paper. Is a plate of ignited platinum capable, then, of condensing and liquefying hydrogen gas? The subject could scarcely admit of experimental investigation without the application of the same useful air-exhauster that was employed with the non-metallic colloids. The metal was always treated in the same manner; so that a description of the details of one experiment will apply to all\*.

Platinum wire or plate being provided, the surface of the metal was first divested of all adhering oily matter, by boiling in caustic alkali and afterwards in distilled water.

The platinum, generally in the form of wire, was then introduced into a porcelain tube M, N (fig. 2), glazed both outside and inside, 0.55 metre in length and 23 millims. in internal diameter. This tube could be heated either by means of the combustion-furnace used for organic analysis, or by placing the tube across the chamber of a small cylindrical furnace. The porcelain tube was fitted at both ends with perforated corks, well cemented with fused gutta serena, and provided each with a small quill tube. Such may be described as the distillatory apparatus employed. It was connected at the end N with the Sprengel pump A B, to be used as an exhauster and transferrer of gas, by means of good caoutchouc adapters (not vulcanized), and at the other end, M, with the apparatus for supplying dry hydrogen, atmospheric air, or any other gas. By a screw clamp upon the adapter at M, the tube could be closed, and the gas-producing apparatus then detached, leaving the porcelain tube shut at one end. A tube of the hard glass used in combustion analysis may be substituted for the porcelain tube in many such experiments. A less degree of heat suffices than was at first supposed.

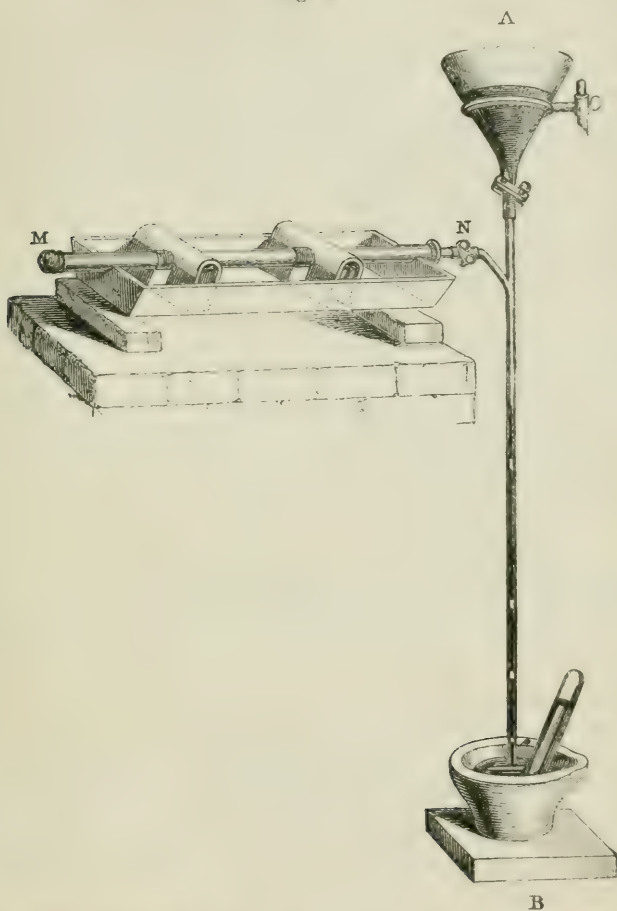
The porcelain tube is exhausted by continuing the action of the Sprengel for ten or fifteen minutes, till small bubbles of gas cease to be delivered by the tube A B in the mercurial trough below. The sufficiency of the joints is thus first ascertained. Heat being then applied to the porcelain tube, its impermeability at a red heat will also be tested.

The platinum, when introduced, was confined to about two-

\* Platinum in the peculiar condition of platinum-black absorbs 745 times its volume of hydrogen gas.—*Traité de Chimie Générale*, par MM. Pelouze et Frémy, vol. iii. p. 398.

thirds of the central portion of the porcelain tube, which could be conveniently heated. The apparatus obviously affords the

Fig. 2.



means both of heating the platinum in a vacuum and also in an atmosphere of hydrogen or any other gas admitted into the interior of the porcelain tube at M.

*Fused platinum.*—Articles of manufactured platinum appear now to be prepared exclusively from the fused metal.

1. A quantity of clean platinum wire from fused metal, measuring 0.695 metre in length, 4.1 millims. in diameter, and 201 grms. in weight, was bent and introduced into the porcelain tube, which was then exhausted. The platinum was first heated

alone for an hour to drive off any natural gaseous product; and then dry hydrogen gas was admitted to the porcelain tube, the gas being evolved from pure sulphuric acid and pure zinc. The hydrogen was conveyed in excess into the porcelain tube, at a cherry-red heat, and the temperature was then allowed to fall in a gradual manner—a procedure which was found to promote the absorption of the gas. The platinum was thus retained for about twenty minutes in an atmosphere of hydrogen, at a temperature partly above and partly below dull redness, terminating with the lower temperature. After the fire was withdrawn and the tube allowed to cool, air or nitrogen was driven through it, and all free hydrogen thus expelled from the apparatus.

The closed tube was now exhausted in the cold, but no hydrogen came off. The platinum being still retained in a good vacuum, heat was again very gradually applied, and the action of the Sprengel pump maintained. Simultaneously with the first appearance of visible ignition, gas began to be evolved. In one hour, the porcelain tube being heated to redness, 2.12 cub. centims. of gas were collected, of which about one-third was collected in the first ten minutes. It was found, by explosion with oxygen, to consist of

Hydrogen . . .	1.93 cub. centim.
Nitrogen . . .	0.19 „

Now, taking the specific gravity of the platinum wire at 21.5, the volume of 201 grms. of metal will be 9.34 cub. centims. Hence one volume of platinum held, the gas being measured cold,

0.207 vol. hydrogen.

The platinum did not appear sensibly altered in lustre, or in any other way, by its relation to the hydrogen.

2. The same piece of platinum wire was drawn out into four times its first length, and the experiment of charging with hydrogen was repeated. The platinum gave up at a red heat, maintained for one hour, 1.8 cub. centim. of gas, of which 1.6 cub. centim. was hydrogen. Here one volume of platinum appears to have held

0.171 vol. hydrogen.

The absorption of hydrogen has not been increased by increasing the surface of the metal.

In two further experiments upon the same platinum wire, the volume of hydrogen retained by one volume of platinum was—

3.	0.173 cub. centim. hydrogen.
4.	0.128 „ „

There is an evident tendency of the hydrogen taken up to diminish in quantity. These experiments have the advantage, for



comparison with the earlier observations on the penetration of a platinum septum by hydrogen gas, that both wire and tube had been drawn out from the same mass of fused metal. No iridium had been added to this platinum, as is sometimes done to increase the elasticity of the metal. The absorption of hydrogen is small, amounting, according to the mean of the four observations, to 17 per cent. of the volume of the platinum. At the temperature of a low red heat, when the absorption took place, the gas would be considerably dilated, to the extent of at least three times its volume stated above, or to about 51 per cent. (half the volume) of the platinum. It is to be considered whether an absorption of half a volume of gas would be sufficient to account for the observed penetration of a septum of metal 1.1 millim. in thickness. The data appear to favour an affirmative conclusion; but their value cannot be very decidedly estimated.

It appears necessary to recognize in platinum a new property, a power to absorb hydrogen at a red heat, and to retain that gas at a temperature under redness for an indefinite time. It may be allowable to speak of this as a power to occlude (to shut up) hydrogen, and the result as the *occlusion* of hydrogen by platinum.

The observation was extended to platinum in other conditions of form, but where, it is to be observed, the metal had not been fused, but only welded, and was not of recent manufacture.

5. Of the grey pulverulent spongy platinum, prepared from the ammonio-chloride, 22.2 grms. were heated by the combustion-furnace, and for half an hour allowed to cool gradually in dry hydrogen gas, as in the preceding experiments. The volume of the platinum is 1.032 cub. centim. by calculation. In the first experiment it yielded to heat and the action of the Sprengel pump 2.2 cub. centims. of a gas which burned like hydrogen. In a second experiment the platinum yielded in one hour (when it appeared to be exhausted) 1.7 cub. centim. of gas, found by explosion to consist of hydrogen 1.52 cub. centim., and nitrogen 0.18 cub. centim. Here one volume of spongy platinum appears capable of occluding

1.48 vol. hydrogen.

6. Wrought platinum, in the form of plate from an old crucible cut up, after washing and ignition, was charged with hydrogen three times in succession. The weight of the platinum was 24.1 grms., and its volume 1.12 cub. centim. It yielded in seventy-five minutes 4.19 cub. centims. of gas, and in thirty minutes further 1.5 cub. centim. more, making together 5.69 cub. centims., of which 4.94 cub. centims. proved to be hydrogen; therm.  $14^{\circ}2$ , barom. 760 millims. Not a trace of carbonic acid was found in the gas before or after explosion. Again, after a

second charge, 5.12 cub. centims. of gas were given up in an hour, of which 4.4 were hydrogen; and lastly, 3.76 cub. centims. in an hour, of which 3.42 were hydrogen. Hence, occluded by 1 vol. wrought platinum—

5.53 vols. hydrogen.

4.93    "       "

3.83    "       "

The volume of occluded hydrogen is much larger than in the fused platinum, or even in the spongy platinum. It exhibits a tendency to fall off on repeating the experiment. The declension in absorbing-power may possibly be connected with the reduced duration of the exposure to hydrogen of the metal while cooling.

7. Wrought platinum, which had been formed many years ago into a small tube, weighing 64.8 grms., 0.322 metre in length and 5 millims. in diameter, was cut into three equal lengths for convenience in placing the metal within the porcelain tube, to be heated and charged with dry hydrogen. By an hour's exhaustion afterwards the platinum yielded 9.2 cub. centims. gas, of which 8.9 were hydrogen. The volume of the platinum itself was 3.9 cub. centims.; and one volume of metal had therefore occluded 2.28 vols. hydrogen, measured at about 20° C. In all such experiments, besides blowing out the free hydrogen by air, the apparatus was also thoroughly exhausted by the Sprengel pump in the cold, before the occluded hydrogen was extracted.

The lustre and appearance of the metallic platinum was not altered by the ingress of the hydrogen; but after the escape of the gas the platinum appeared whiter in colour, and the surface was covered by minute blisters.

Repeating the experiment, the gas collected by an hour's exhaustion was 8.7 cub. centims., of which 8.46 cub. centims. were hydrogen. Here the metal occluded 2.8 vols. of hydrogen.

The same platinum was a third time charged with hydrogen; but on this occasion the platinum was placed in a tube of hard glass, and the tube connected with the air-exhauster. The glass tube was heated by an oil-bath, and the platinum kept *in vacuo* at a temperature of 220° C. for an hour. Not a bubble of gas was evolved. The glass tube was afterwards heated by a small Bunsen burner, which was calculated to give a degree of heat little short of visible redness; still no hydrogen came off. The tube was now heated sufficiently to soften glass (500°). Gas began to come off, of which 1.8 cub. centim., containing 1.72 hydrogen, were collected in ten minutes. The glass tube having cracked, the whole apparatus was allowed to cool, and the platinum transferred to a porcelain tube. Further heated by a com-

bustion-furnace for one hour, the platinum gave off 8.6 cub. centims. gas, of which 8.2 were hydrogen. The platinum therefore appears to have occluded altogether 3.79 vols. of hydrogen.

The preceding experiment appeared to show a complete sealing up of the occluded hydrogen at low temperatures, seeing that, although nearly four volumes of gas were present, none escaped below a red heat. But to test the effect of time at the temperature of the atmosphere, the platinum, again charged with hydrogen, was sealed up hermetically in a glass tube, which it nearly filled, and not opened for two months. The air in the tube was then transferred and examined. It did not exhibit any reduction of volume under the electric spark or a pellet of spongy platinum. The air therefore appeared to contain no hydrogen; the latter had not diffused out, but, it is to be presumed, was retained by the platinum without loss. These experiments, although related last, were the first performed in this inquiry. The included hydrogen was never entirely extracted in an hour, and is probably understated. The gas always came off gradually, more than one-half of the whole in the first twenty or thirty minutes. The last results may be stated as follows:—

1 vol. hammered platinum occluded 2.28 vols. hydrogen.

”	”	”	2.80	”
”	”	”	3.79	”

The high absorbing-power of the hammered platinum, or rather the low absorbing-power of the fused metal, was ascribed to a mechanical difference between the two—to a more open texture in the former, permitting more free access of hydrogen liquefied, as it may be, to the interior of the metal.

8. The extrication of occluded hydrogen from platinum had always required a degree of temperature verging upon a red heat, even when aided by a vacuum; and this remains true of hydrogen originally absorbed at or near a red heat. But the fact appears to be compatible with the absorption of the gas, under the pressure of the atmosphere, at a considerably lower temperature. Thin platinum-foil was first deprived of a little natural gas by ignition *in vacuo* in the porcelain tube. The foil was afterwards placed in a glass tube and heated again in a stream of hydrogen to a temperature not exceeding 230° C., for three hours, by means of an oil-bath, and further allowed to cool slowly in an atmosphere of the same gas for several hours. A second glass tube receiver, to which the platinum-foil was transferred, was exhausted, as usual, at 20° C. without any sensible evolution of gas. With a red heat superadded, gas came off in twenty minutes (but nearly all in the first seven minutes) to the extent of 0.75 cub. centim., of which 0.56 cub. centim. proved to be hydrogen.



The volume of 8.3 grms. of platinum is 0.385 cub. centim. Hence one volume of platinum-foil appears to take up, in three hours,

1.45 vol. hydrogen at 230° C.

9. The same portion of platinum-foil was again charged with hydrogen at a still lower temperature, namely between 97° and 100°, for three hours. Submitted to exhaustion at a red heat, the platinum now gave off 0.5 cub. centim. of gas in thirty-five minutes, of which about 0.3 cub. centim. were hydrogen. One volume of platinum-foil had taken up

0.76 vol. hydrogen at 100°.

By this property platinum is connected with palladium, which of all metals appears to possess the power of absorbing hydrogen in the highest degree.

### *Palladium.*

Of late years palladium has become comparatively uncommon; and some difficulty was experienced at first in procuring more than a gramme or two of the metal, in the form of thin foil. The palladium-foil first employed weighed 1.58 grm., and measured 0.133 cub. centim. (taking the specific gravity of the metal at 11.86), and had a surface of 0.00902 square metre. It gave off, when heated *in vacuo* for one hour, 1.50 cub. centim. of natural gas, containing no compound of carbon, but consisting of hydrogen and air.

1. As it appeared from preliminary experiments that the occlusion of hydrogen by palladium was likely to be a phenomenon exhibited at a comparatively low range of temperature, the metal was heated in hydrogen no higher than 245° C., by an oil-bath, and allowed to cool very slowly, so as to pass through still lower ranges of temperature which might be favourable to the absorption of hydrogen. The metal, when afterwards transferred to the distillatory glass tube, appeared to give out nothing to a vacuum at 17° 8 C. and barom. 759 millims. But the moment the combustion-furnace was lighted under the tube, gas came off most freely. Of the first portion collected, 11.77 cub. centims. contained 11.74 cub. centims. hydrogen. The gas ceased to be evolved in fifteen minutes, when 69.92 cub. centims. were collected, of which the greater part came over in the first ten minutes. Hence palladium had taken up a large volume of gas when the temperature of the metal never exceeded 245° C.

1 vol. palladium held 526 vols. hydrogen.

2. In a similar experiment the temperature of absorption was still further lowered with good effect. The palladium was ex-



posed to hydrogen between  $90^{\circ}$  and  $97^{\circ}$  C. for three hours, and then allowed to cool in the gas for one hour and a half. Now placed in a glass tube, exhausted, and heated by a gas-flame, the palladium gave off gas in a continuous stream for twelve minutes, when it ceased. The gas amounted to 85.56 cub. centims., of which 96.8 per cent. was hydrogen; therm.  $17^{\circ}5$ , barom. 764 millims.

1 vol. palladium held 643.3 vols. hydrogen.

By the care of my zealous assistant, Mr. W. C. Roberts, the hydrogen employed in these experiments was purified to the highest degree by passing it in succession through alcohol, water, caustic potash, and tubes of 0.7 metre each, filled with broken glass impregnated with nitrate of lead, sulphate of silver, and oil of vitriol. The gas was inodorous, and burned with a barely visible flame.

No alteration was sensible in the metallic appearance of the palladium-foil when charged with hydrogen, or when discharged. The foil was much crumpled and rather friable after repeated use; but this may have arisen from frequent handling.

3. Palladium appears to absorb hydrogen largely, even at natural temperatures, provided that the metal has been recently ignited *in vacuo*. The foil, without such preparation, was placed in a bottle of pure hydrogen for several hours, but yielded nothing when afterwards ignited in the Sprengel vacuum. The foil, however, being immediately returned after cooling to a stoppered bottle containing hydrogen, and left in the gas for a night, absorption now took place—air rushing in, on opening the stopper, as into a partial vacuum; therm.  $19^{\circ}$ . When the palladium-foil was afterwards transferred to a glass tube and connected with the Sprengel pump, it was found difficult to obtain a vacuum for some time, owing to hydrogen coming off at the temperature of the atmosphere. But after a fair vacuum was produced 6.96 cub. centims. were collected, of which 6.78 proved to be hydrogen. Heat was then applied, and 42 cub. centims. came over in five minutes, making altogether more than 50 cub. centims., or 376 volumes of gas. The absorption of hydrogen appears, then, to be suspended at a low temperature, unless the condition of the metal be favourable. The action of a plate of clean platinum in determining the combustion of explosive gas is equally critical at a low temperature.

4. A different specimen of palladium-foil, weighing 5.76 grms., and having a volume of 0.485 cub. centim., was charged with hydrogen, and discharged, more than once. In the second experiment, the foil was heated in hydrogen at  $100^{\circ}$  for three hours. Distilled afterwards in a porcelain tube at a low red heat in the

usual way, the palladium was found to have absorbed, at  $100^{\circ}$ ,  
 347.7 vols. of hydrogen measured at  $18^{\circ}2$  C. and barom.  
 756 millims.

5. So large an absorption of hydrogen should increase the weight of the palladium sensibly, notwithstanding the lightness of the gas. One litre, or 1000 cub. centims., of hydrogen at  $0^{\circ}$  C. and 760 millims. weighs 0.0893 grm. Of new palladium-foil, believed to be from *fused* metal, 5.9516 grms. increased to 5.9542, or by 0.0026 grm., when the metal was charged with hydrogen at  $100^{\circ}$  for four hours. This amounts to only 29.01 cub. centims. of hydrogen at  $0^{\circ}$  C. and 760 millims. barom. The gas actually extracted afterwards from the palladium did not exceed 34.2 cub. centims. at  $19^{\circ}$  C., and barom. 758 millims., equivalent to 31.84 cub. centims. at  $0^{\circ}$  C. and 760 millims. barom. The whole gas extricated (68 vols.) seems unusually small, but it corresponds closely enough with the volume calculated from the increase of the palladium in weight. An inferior absorbing-power for hydrogen appears to be connected in both platinum and palladium with the fusion of the metal.

6. A portion of similar palladium-foil, charged with hydrogen, was found to have its gas reduced from 20.7 to 16.2 cub. centims. after exposure to the air for forty-two hours. The liquid hydrogen, whether held by the substance or in the pores of the metal, appears therefore to evaporate slowly at the temperature of the atmosphere, therm.  $19^{\circ}$ , barom. 752 millims.

7. Spongy palladium, from the ignition of the cyanide, being heated in hydrogen at  $200^{\circ}$ , and allowed to cool slowly in the same gas for four hours, the metal was found to have taken up 686 vols. of hydrogen.

Treated in a similar manner with air, spongy palladium exhibited no absorbing-power for oxygen or nitrogen.

Hydrogen, condensed either in the palladium sponge or foil, was observed to have its chemical affinities enhanced. The palladium being placed in dilute solutions of the following substances for twenty-four hours in the dark at the ordinary temperature, the action of the hydrogen became manifest.

Persalt of iron became protosalt.

Ferri-cyanide of potassium became ferrocyanide.

Chlorine-water became hydrochloric acid.

Iodine-water became hydriodic acid\*.

Apart from hydrogen, the palladium sponge exhibits a power

\* The power of platinum-black charged with hydrogen to communicate the latter element to organic compounds has lately been observed by M. P. de Wilde, following Dr. Debus.—*Bulletin de la Société Chimique*, March 1866.

of selection and absorption of alcohol in preference to water. 30 grms. of the sponge were left in contact with 9.5 cub. centims. of dilute alcohol of specific gravity 0.893, for fifty-one hours, in a sealed tube. The supernatant liquid now drawn off to the extent of 3.9 cub. centims. was of specific gravity 0.901, while the portion retained by the palladium was found when distilled to be of specific gravity 0.885, or it was sensibly concentrated. This chemical action of palladium sponge was more than once verified. Platinum sponge, on the other hand, exhibited no indication of a similar separating-power; nor did the sponge of iron reduced by hydrogen from the oxide.

8. Connected, it may be, with this chemico-molecular action of palladium is the variable absorptive power for different liquids exhibited by palladium-foil. Immersed in various liquids for an hour, and afterwards dried by pressure for a few seconds between folds of blotting-paper, a quantity of palladium-foil represented by 1000 was found to retain in its pores—

Of Water . . . . .	1.18 part.
Of Alcohol (0.802) . . . .	5.5 parts.
Of Ether . . . . .	1.7 part.
Of Acetone (0.794) . . . .	0.54 „
Of Glycerine . . . . .	4.5 parts.
Of benzol . . . . .	3.5 „
Of Oil of sweet almonds . .	18.1 „
Of Castor-oil . . . . .	10.2 „

The superior penetrativeness of alcohol over water is well marked; capillary action appears to merge into a chemical affinity. Liquid hydrogen would also appear as highly absorbable by palladium-foil. It would appear also to be separable from other gases (or liquids), as alcohol is from water, by the palladium-pores.

*Alloy of 5 palladium and 4 silver.*—The power to absorb hydrogen appears to extend to this alloy of palladium. A plate of the alloy, about 180 millims. in length, 31 millims. in width, and weighing 74.3 grms., was bent, so as to be able to enter a wide porcelain tube that could be exhausted of air when required. The volume of the palladium alloy was 6.21 cub. centims. The plate of metal being placed in the porcelain tube, had hydrogen gas passed over it at a low red heat for one hour, and was then allowed to cool slowly in the same gas. Taken out and examined, the metal was not visibly altered. For the extrication of gas the metal was distilled in the porcelain tube heated by jets of gas, and connected with the Sprengel pump, as usual. In seven minutes after the gas-furnace was lit, 24 cub. centims. of gas came off; in ten minutes more, 80.71 cub. centims.; and in



seventy-five minutes more, 36.75 cub. centims., making altogether 141.46 cub. centims. Of this gas 127.74 cub. centims. proved to be hydrogen, the remainder being nitrogen, derived, no doubt, from the large imperfectly exhausted porcelain tube. The palladium alloy, in the form of a thick plate, appears therefore to have held

20.5 vols. hydrogen, measured at  $18^{\circ}2$  and barom. 756 millims.

This alloy of palladium becomes crystalline by heating, and appears to lose much of its absorbent power at the same time.

The conclusion, then, is that welded palladium, in the condition of thin foil, readily absorbs hydrogen, to the extent of upwards of 600 times the volume of the metal at a temperature under the boiling-point of water, upwards of 500 volumes at  $245^{\circ}$ , and less at higher temperatures, the metal being always surrounded by hydrogen under atmospheric pressure. Hydrogen is also largely absorbed, although less constantly, at ordinary temperatures. On the other hand, palladium already fully charged with hydrogen at or under  $100^{\circ}$ , and under the pressure of the atmosphere, begins to give out gas when exposed either to atmospheric air or to a vacuum at the original temperature of absorption; and the gas is freely discharged at  $200^{\circ}$  C.

It is probable that hydrogen enters palladium in the physical condition of liquid, whether the phenomenon prove to be analogous to the imbibition of ether, chloroform, and such solvents by the colloid india-rubber, or whether a certain porosity of structure in the palladium be required. The porosity of the metal is supposed to be of that high degree which will admit liquid but not gaseous molecules. Now the numerous liquid compounds of carbon and hydrogen have all a nearly similar density, generally a little under that of water. There is no reason to suppose that the density of liquid hydrogen would differ greatly from the hydrocarbon class; but then the surprising lightness of hydrogen gas must cause liquid hydrogen to yield a volume of vapour disproportionately large when compared with the former class of substances, or, indeed, with any other substance whatever. The absorption of hydrogen by palladium will appear, then, less extravagantly great when viewed as the absorption of a highly volatile liquid capable of yielding an exceedingly light vapour, rather than that of a gas.

An excellent opportunity of observing the penetration by hydrogen of a compact plate of palladium, 1 millim. in thickness, was afforded by a tube of that metal constructed by Mr. Mathey. This tube was said to have been welded from palladium near the point of fusion of the metal. The length of the tube was 115 millims., its internal diameter 12 millims., thickness 1 millim.



and external surface 0.0153 of a square metre. It was closed by thick plates of platinum soldered at both ends, one of the plates being perforated by a long small tube of platinum, by which the cavity of the palladium tube could be exhausted of air.

Now the closed palladium tube remained air-tight, when exhausted by the Sprengel tube at the ordinary temperature, at  $260^{\circ}$ , and at a temperature verging on low redness, the gas without being atmospheric air. Hydrogen being then substituted as the external gas, the walls of the palladium tube still remained impermeable at a low temperature. No hydrogen gained the interior in three hours at  $100^{\circ}$ . But the temperature being gradually raised by means of an oil-bath to  $240^{\circ}$ , hydrogen then began to come through, and at a gradually increasing rate to  $265^{\circ}$ . The hydrogen then entered steadily at the rate of 8.67 cub. centims. in five minutes. This gives a rate of 327 cub. centims. for a square metre of surface per minute. Heated to a temperature just short of redness, the passage of hydrogen was increased to 11.2 cub. centims. in five minutes, or 423 cub. centims. for a square metre per minute.

With coal-gas as the external atmosphere the penetration of the palladium began about the same temperature, and was continued at  $270^{\circ}$  at the rate of 57 cub. centims. for a square metre of surface per minute. The penetrating gas had no odour of coal-gas, contained no trace of carbon, and appeared to be absolutely pure hydrogen. The exact isolation of the latter gas by septa of both platinum and palladium appears most extraordinary.

A quantitative determination of the hydrogen in a gaseous mixture could probably be effected by means of the hollow cylinder of palladium.

Is the power to penetrate the metals in question confined to hydrogen? It has been lately concluded by Dr. C. Wetherill that the turgescence of the ammonium amalgam depends entirely upon the retention of hydrogen gas-bubbles\*; hydrogen, then, appears to exhibit an attraction of a peculiar kind for mercury. The ready liquefaction of the same gas by the platinum metals evinces also a powerful mutual attraction. The only other volatile body which has been observed to pass, like hydrogen, through a plate of palladium is common ether—and that at the atmospheric temperature, while a passage was denied to hydrogen at the same time. The palladium was in the form of foil. Although thin foil of this metal is generally visibly porous and allows air to pass through like a sieve, a tube diffusimeter, covered with a disk of the selected palladium-foil, and standing over mercury, retained a volume of 40.5 millims. of air over a vertical column of 155 millims. of mercury for twenty-fours without depression

\* *American Journal of Science*, vol. xlii. No. 124.

of the mercury. The air was dried by sticks of potash; but still it did not penetrate the palladium. Dry hydrogen was then conducted to the upper surface of the palladium disk, but still without any penetration by that gas after several hours. Cotton-wool moistened with ether was now placed upon the disk, when, after eight minutes, the confined air within the tube began to expand; and in the course of an hour longer, the 40.5 volumes of confined air increased to 90.4 (thermometer  $18^{\circ}5$ , barometer 758), when the expansion ceased. The increase of volume appeared to be due entirely to ether-vapour, absorbable by a pellet charged with sulphuric acid. Why hydrogen proved to be incapable of penetrating the palladium in such circumstances it is difficult to say. It can only be imagined that the palladium-foil may have previously condensed on its surface a minute film of foreign matter, which rendered the palladium inactive to hydrogen but not to ether-vapour.

On the other hand, the penetrating power of hydrogen, here referred to the liquefaction of that gas, appears not to be solely confined to metallic septa. There is reason to suspect that in diffusing through a plate of graphite hydrogen passes in a small proportion as a liquid, without any counterdiffusion of air. Hence the constant excess observed of the diffusive coefficient of hydrogen, which came out 3.876, 3.993, and 4.067\*, instead of the theoretical number 3.8, corresponding to the density of the gas referred to air. Such phenomena of gaseous penetration suggest a progression in the degree of porosity. There appear to be (1) pores through which gases pass under pressure or by capillary transpiration, as in dry wood and many minerals, (2) pores through which gases do not pass under pressure, but pass by their proper molecular movement of diffusion, as in artificial graphite, and (3) pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite.

#### *Osmium-iridium.*

A portion of small grains of osmium-iridium, amounting to 2.528 grms., was exposed to hydrogen through all descending temperatures from a red heat, as the preceding metals had been treated. The osmium-iridium was then heated again to redness in the Sprengel vacuum, to extricate any hydrogen that might have been absorbed. But only a bubble or two of gas, too minute to be measured, passed over in 15 minutes, at a red heat. Osmium-iridium, then, exhibits no absorbent power

\* Philosophical Transactions, 1863, p. 404.

for hydrogen—a result which is consistent with the crystalline character of the substance.

### Copper.

The power to occlude gases appears not be confined to palladium and platinum among the metals. The exact experiments of M. Dumas, by which the atomic weights of the leading elements were definitely settled, afford an indication of the absorption of hydrogen gas by spongy metallic copper reduced from the oxide, sufficient to affect the weight of the metal to the extent of about 3 parts in 100,000\*.

1. With the view of applying the method of extracting gas followed in the treatment of the preceding metals, so much oxide of copper was reduced by hydrogen as was calculated to yield 50 grms. of metallic copper. The reduced metal was again heated to redness and slowly cooled in a stream of dry hydrogen. After free exposure to the air for a few minutes, the metal was now submitted, at a red heat, to the action of the Sprengel pump. It then gave off in one hour 3.35 cubic centims. of gas, measured cold, which appeared to be pure hydrogen (the explosion with oxygen indicated 3.4 hydrogen). Taking the specific gravity of copper at 8.85, 50 grms. of that metal would be 5.65 cub. centims. in volume, and the result is that

1 vol. reduced copper sponge occludes 0.6 vol. hydrogen.

Hydrogen being about 12,000 times as light as copper (at 15°), 1 part of gas by weight has been taken up by 20,000 parts of metal.

2. The same weight and volume of fine copper, in the form of wire thoroughly cleaned, was exposed to hydrogen at a red heat, and then submitted to exhaustion for one hour. It gave 2.6 cub. centims. gas, of which 2 cub. centims. were hydrogen, and the remaining 0.6 principally carbonic oxide. It may be represented that

1 vol. wrought copper occludes 0.306 vol. hydrogen.

Where a metal, such as wrought copper, may contain small quantities of carbon and oxygen, an obvious cause will exist for the production and evolution of carbonic oxide under the influence of heat. Gas so generated appears to be added to the occluded hydrogen when extricated in the last experiment.

\* *Annales de Chimie et de Physique*, 3 sér. vol. viii. p. 205. The observations of M. Melsens show that 240 grms. of copper may fix about 0.007 grm. of hydrogen, most being fixed when the oxide of copper is reduced by hydrogen at a low temperature. In the subsequent oxidation of the copper the gas does not come out suddenly, but in a gradual manner.

*Gold.*

1. A quantity of gold was precipitated from the assay cornettes used below by means of oxalic acid. The gold weighed 93·3 grms., with a volume of 4·83 cub. centims., taking the specific gravity of the metal as 19·31. Exhausted at a red heat without any further treatment, the reduced gold yielded 3·4 cub. centims. of gas, which may therefore be supposed to be gas usually present in gold reduced in the manner described. This is 0·704 vol. of the gold. The occluded gas in precipitated gold gave to analysis

0·05	cub. centim.	Oxygen.
1·50	„ „	Carbonic acid.
1·85	„ „	Carbonic oxide &c.
<hr/>		
3·40		

2. Of the original cornettes of fine gold, from gold-assays conducted several months before, 93·3 grms., having a volume of 4·83 cub. centims., were submitted without any further treatment to aspiration at a red heat. The gold gave up in the first half hour 9·45 cub. centims. of gas, and in the second half hour 0·8 cub. centim., making together 10·25 cub. centims. Hence 1 volume of the gold cornettes appears to hold 2·12 volumes of gas. This gas consisted of.

6·70	cub. centims.	Carbonic oxide.
1·50	„ „	Carbonic acid.
1·58	„ „	Hydrogen.
0·44	„ „	Nitrogen.
0·03	„ „	loss.
<hr/>		
10·25		

The cornettes do not appear ever to assume again so much gas as they first acquired in the assay muffle. It follows that the weight of a gold cornette is increased about 2 parts in 10,000 by the weight of occluded gas. As the gold also retains 7 or 8 parts of silver in 10,000, it follows that the absolute quantity of gold in a cornette is less than the weight of the cornette as indicated by the balance by 1 part in 1000. This does not disprove the accuracy of the usual gold-assay, which is always made in comparison with gold of known composition as a check, and is therefore *relatively* true.

3. The same volume of gold cornettes, amounting to 4·83 cub. centims., heated again in carbonic oxide gas, gave up afterwards 1·6 cub. centim. of occluded gas composed of

1·4	cub. centim.	Carbonic oxide.
0·2	„ „	Carbonic acid.
<hr/>		
1·6		



4. The same mass of gold cornettes heated in hydrogen gas gave up afterwards in one hour 2·7 cub. centims. of gas, which appeared to consist of

2·34	cub. centims.	Hydrogen.
0·36	„ „	Nitrogen &c.
2·70		

The power of this metal to occlude hydrogen gas is very sensible. The metal here appears to hold 0·48 volume of hydrogen gas. The same gold, when dissolved and precipitated, was also found capable of holding 0·44 volume of hydrogen.

5. The same mass of cornettes, heated in carbonic acid gas, gave up afterwards in one hour 1·05 cub. centim. gas in which baryta-water showed the presence of

0·78 cub. centim. Carbonic acid.

The charged cornettes were always freely exposed to air for some time before occluded gas was extracted from them and measured, so as to allow the escape of any loosely attached gas.

6. The same cornettes were heated and cooled in a stream of dry air, in like manner as they had been treated with other gases. The occluded air given out in one hour amounted in two different experiments to 1·15 and 0·95 cub. centim. respectively. The gas of the second experiment gave

0·82	cub. centim.	Nitrogen	.	=	86·3
0·08	„ „	Carbonic acid		=	8·4
0·05	„ „	Oxygen	.	=	5·3
0·95					100·0

The whole occluded air amounts to 0·2 volume of the gold, and is principally *nitrogen*. The indifference of gold to oxygen is remarkable, and contrasts with the power of silver to occlude the same gas.

### *Silver.*

1. Fine silver in the form of wire, 2 millims. in diameter, with its surface duly purified, was first heated alone in the porcelain tube, and then exhausted of gas by the Sprengel tube in the usual way. The natural gas derived from this metal was small in quantity, and it appeared to come off almost entirely in one hour. The silver wire weighed 108·8 grms., and had a volume of 10·37 cub. centims., taking the specific gravity of pure silver as 10·49. The gas extracted amounted to

2·2	cub. centims.	in thirty minutes.
0·8	„ „	„
3·0	„ „	in one hour.

The gas consisted of

2.4	cub. centims.	Carbonic acid.
0.6	„ „	Carbonic oxide.
<hr/>		
3.0		

Silver wire therefore appeared to hold occluded 0.289 volume of gas, principally carbonic acid. There is reason, however, to suppose that the occluded gas may really be oxygen, and that the latter was converted into carbonic acid at the temperature of extrication, by a trace of carbon existing in the fine silver.

2. The same quantity of silver wire was now charged with hydrogen, by being heated to redness and afterwards cooled slowly in that gas. The gas extricated amounted to

2.3	cub. centims.	in forty-five minutes.
0.2	„ „	in fifteen minutes.
<hr/>		
2.5	„ „	in one hour.

The gas consisted of

2.2	cub. centims.	Hydrogen.
0.3	„ „	Nitrogen, &c.
<hr/>		
2.5		

The fine silver had therefore occluded 0.211 volume of hydrogen. The metal acquired a beautiful frosted appearance on the surface; and by repeated heating it became highly crystalline and brittle.

3. The same portion of silver was now charged with oxygen. The occluded gas given off amounted to

7.5	cub. centims.	in thirty minutes.
0.3	„ „ „	
<hr/>		
7.8	„	in one hour.

The gas consisted of

7.6	cub. centims.	Oxygen.
0.2	„	Nitrogen, &c.
<hr/>		
7.8		

The silver therefore held occluded 0.745 volume of oxygen. This gas, like the hydrogen in platinum, was permanently fixed in the metal at all temperatures below an incipient red heat. It did not tarnish the bright metallic surface of the silver, or produce any appearance suggestive of the oxidation of a metal.

4. The same portion of silver, after being dissolved in acid, precipitated as chloride, and reduced again, was exposed to atmospheric air at a red heat, and afterwards exhausted. The gas

given off amounted to

5.56 cub. centims. in fifteen minutes.

0.30	"	"	"
5.86			

Of this gas 5.56 cub. centims., or nearly the whole, proved to be oxygen gas; or the silver held occluded 0.545 volume of oxygen. This silver had been purified from the chloride, and it contained no trace of copper.

When silver, of British standard (that is, containing 7.5 per cent. of copper), is exposed to air or oxygen at a low red heat, the silver becomes almost black on the surface from oxidation of the copper. Silver wire in this blackened state gave off several volumes of oxygen under the action of heat and a vacuum. Much of the superficial oxide disappeared at the same time. It appeared as if the operation tended to the reduction of the superficial oxide of copper, oxygen being liberated, and the copper absorbed by the mass of silver.

5. A specimen of silver reduced from the oxide, in the form of sponge, which was considered pure, but was not analyzed, occluded 6.15, 8.05, and 7.47 volumes of oxygen, in successive experiments, without any visible tarnish of the surface. Can the attraction or affinity of silver for oxygen, which enables the pure metal to occlude that gas, be enhanced by the presence of a mere trace of some positive metal like copper?

6. The same specimen of fritted silver was found to occlude, in successive experiments,

0.907 vol. Hydrogen.

0.938

" "

0.486 " Carbonic acid.

0.545

" "

0.156 " Carbonic oxide.

Hydrogen and carbonic acid, as well as oxygen, appear to be taken up in larger proportion by this silver than by the former specimen of the same metal.

7. Of pure silver highly laminated, 500 leaves, weighing 12.5 grms., were exposed to air at a red heat, and thereafter exhausted at the same temperature. The silver (1 vol.) gave up 1.37 volume of oxygen, 0.20 volume of nitrogen, and 0.04 volume of carbonic acid.

It appears that silver has a relation to oxygen similar to that exhibited by platinum, palladium, and iron to hydrogen. The power of silver and of litharge in a state of fusion to absorb oxygen, and to allow that gas to escape on solidification, may be connected with the observed capacity of the colloid metal, softened by heat, to absorb the same gas, although to a less extent.

*Iron.*

The penetration of iron by hydrogen is demonstrated as clearly by MM. Deville and Troost as that of platinum. A thin tube of cast steel, 3 or 4 millims. in thickness, already enclosing hydrogen gas in its cavity, was surrounded by air or by nitrogen gas circulating in an annular space between the steel tube mentioned and a wider external porcelain tube. In the absence of any visible pores in the steel, hydrogen made its way through the substance of the metal, and escaped into the annular space as soon as the system of tubes was exposed to a red heat. A nearly if not entirely complete vacuum was formed within the iron tube\*. In another modification of the experiment, carbonic oxide from an uncertain source appeared within the iron tube, particularly when the temperature was most elevated†.

Wrought iron, in the form of thin wire (No. 23), about 0.4 millim. in diameter, first carefully cleaned with caustic alkali and water, was heated alone in the porcelain tube exhausted of air, for the purpose of eliminating any natural gases.

1. Of the iron wire referred to, 46 grms., with a volume of 5.9 cub. centims., the specific gravity of the metal being taken at 7.8, were heated by the open combustion-furnace. Gas came off freely at a red heat,—

(1) In fifteen minutes, 15.6 cub. centims., containing 3.5 cub. centims. carbonic acid, or 22.4 per cent.

(2) In fifteen minutes, 7.17 cub. centims., containing 0.52 cub. centim. or 7.2 per cent. of carbonic acid. The gas of this and the following stages of observation now burnt with a blue flame, and was principally carbonic oxide.

(3) In thirty minutes, 10.4 cub. centims., of which 6.86 cub. centims. were carbonic oxide.

(4) In thirty minutes, 8.16 cub. centims., of which 0.12, or 1.4 per cent., was carbonic acid.

(5) In thirty minutes, 5.52 cub. centims., of which 0.3 was carbonic acid—that is, 0.5 per cent.

Hence 46 grms. of wrought iron have in two hours given off 46.85 cub. centims. of gas, measured at about 15°C.; or 1 volume of iron has discharged 7.94 volumes of gas, of which about two-thirds was carbonic oxide; and the metal does not appear to be yet quite exhausted. Iron is a metal not unlikely to contain small quantities of carbon and oxygen, both in chemical union with iron; and the gas extricated may partly be due to a reaction of these elements upon each other at a red heat.

2. In another, similar experiment upon 32 grms. of clean iron

\* *Comptes Rendus*, vol. lvii. p. 965 (1863).

† *Ibid.* vol. lix. p. 102 (1864).



wire (No. 21), measuring 4.1 cub. centims., the iron was heated in a small glass tube, to exclude the idea of the conceivable permeability of the porcelain tube. The iron gave off gas at a pretty uniform rate, which amounted in an hour to 29.8 cub. centims., of which 4.44 cub. centims. were carbonic acid, and the remainder principally carbonic oxide, with hydrogen and a trace of a hydro-carburet. Here the iron wire gave off 7.27 volumes of gas.

3. In a third experiment, on thin iron wire (No. 23), the extrication of the natural gases at a red heat was pushed to a greater degree of exhaustion. The weight of the iron was 39 grms., and its volume 5 cub. centims. In the first and second hour the gas collected was 45 cub. centims.; in the third hour 10.85 cub. centims.; in the fourth and fifth hours 5.65 cub. centims.; in the sixth hour 0.9 cub. centim., and in the seventh hour 0.7 cub. centim. The iron appears to be now nearly exhausted, after the extrication of 63.1 cub. centims., or 12.55 volumes of gas.

It is evident that iron cannot be safely dealt with in experiments upon the permeation or upon the absorption of gases, till these gases, whether self-produced or preexisting, are first extricated from the metal. The carbonic oxide observed in the tube experiments of M. Deville may have been derived from the same source\*.

4. To observe the absorption of hydrogen, the mass of exhausted iron wire remaining after the last experiment was heated to redness, and cooled gradually in the same gas. The metal was afterwards freely exposed to air (as usual) to get rid of any loosely attached hydrogen. Now exhausted again by the Sprengel pump at a low red heat, the iron gave 2.5 cub. centims. of gas in one hour, but the greater portion in the first ten minutes, consisting of

2.3 cub. centims.	Hydrogen.
0.2	„ Carbonic oxide &c.
2.5	

The iron appears therefore to be capable of holding 0.46 volume of hydrogen. The wire became white, like galvanized iron. This was confirmed in a second observation, a thicker wire holding 0.42 vol. hydrogen.

5. The same specimen of iron was now charged with carbonic oxide gas, in the manner it had previously been charged with hydrogen. It was also freely exposed to air. The iron wire remained soft, was not capable of becoming hard when heated red-

\* The gases which escape from cast iron in a state of fusion have been examined by M. L. Cailltet. They appear to contain from 49 to 58 per cent. of carbonic oxide, 34 to 39 of hydrogen, and 8 to 12 of nitrogen.—*Comptes Rendus*, vol. lxi. p. 850 (1865).

hot and suddenly cooled, and was not altered in aspect or in solubility in acids. The gas extricated by the air-exhauster amounted to

9.45	cub. centims.	in 13 minutes.
2.43	„	5 „
8.05	„	42 „
3.15	„	60 „
<u>23.08</u>	„	in two hours.

Of this gas 20.76 cub. centims. proved to be carbonic oxide. *Pure iron, then, is capable of taking up at a low red heat, and holding when cold, 4.15 volumes of carbonic oxide gas.* This fact was confirmed in various other experiments. It explains partly, if not entirely, the abundance of carbonic oxide observed among the natural gases of iron in experiments 1, 2, and 3. In the course of its preparation wrought iron may be supposed to occlude six or eight times its volume of carbonic oxide gas, which is carried about ever after. How the qualities of iron are affected by the presence of such a substance, no way metallic in its characters, locked up in so strange a way, but capable of reappearing, under the influence of heat, at any time, with the elastic tension of a gas, is a subject which metallurgists may find worthy of investigation.

The relations of the metal iron to carbonic oxide gas appear to be altogether peculiar. They cannot fail to have a bearing upon the important process of *acieration*. The intervention of carbonic oxide in the usual process of the cementation of iron with charcoal, long recognized by accurate observers, may be said now to be placed beyond all doubt by the recent beautiful research of M. Margueritte\*. Hitherto the decomposing action of the iron upon carbonic oxide has been supposed to be exercised only at the external surface of the metal. A surface-particle of the iron has been supposed to assume one-half of the carbon belonging to an equivalent of carbonic oxide ( $C^2O^2$ ), while the remaining elements diffused away into the air as carbonic acid ( $CO^2$ ), to reacquire carbon from the charcoal placed near, and to become capable of repeating the original action. It is now seen that such a process need not be confined to the surface of the iron bar, but may occur throughout the substance of the metal, in consequence of the prior penetration of the metal by carbonic oxide. The direct contact and action of carbon (in the form either of diamond or charcoal) upon iron is allowed to produce cast iron and not steel. It appears that the diffused action of carbonic oxide is the proper means of distributing the carbon throughout the mass of iron. The blistering of the bar appears to testify to the necessary production and evolution of carbonic

\* *Annales de Chimie*, &c. 4 sér. vol. vi. 1865.

acid, owing to the decomposition of the carbonic oxide in the interior of the bar.

The inquiry suggests itself whether acieration would not be promoted by alternation of temperature frequently repeated. The lowest red heat, or a temperature even lower, appears to be most favourable to the absorption of carbonic oxide by iron, or for impregnating the metal with that gas; while a much higher temperature appears to be required to enable the metal to decompose carbonic oxide, to appropriate the carbon and become steel. The action of a high temperature is made very clear by M. Margueritte. The process of acieration, it seems then, should be divided into two distinct stages, conducted at very different temperatures,—the first to introduce carbonic oxide into the iron, and the second to decompose the carbonic oxide so introduced. The carbonic oxide once safely occluded by the iron, the metal might even be cooled and preserved in the air, the second heating being postponed for any length of time. Such alternations of temperature are not unlikely to occur by accident during the usual long process of cementation; but they might be properly regulated with advantage, and the process may admit of being abridged in point of time.

Antimony, as a highly crystallizable metal, was exposed to hydrogen gas both above and below the point of fusion of the metal, and afterwards submitted to exhaustion in the usual manner. No hydrogen was extricated.

## LXX. *Remarks on the Nature of Æther.*

By CHARLES BROOKE, M.A., F.R.S.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

I BEG leave to forward to you for insertion in your valuable Journal a few paragraphs on the physical properties of æther, about to be inserted in the beginning of my first chapter on Light, thinking that they may interest many of your readers, who would never dream of dipping into the pages of a professedly elementary work, for the remote chance of finding some idea with which they were not already familiar; and I do so the more willingly because I desire to court investigation of an important point in physics from those who are more competent than most of my ordinary readers to entertain the question at issue.

That some material medium pervades infinite space, as the means of transmission of the light- and heat-waves (as the case may be) of the heavenly bodies, is indispensable to the dynamical theory; but is it equally, or indeed at all, necessary to imagine that the portion of space within the confines of our atmosphere, which is occupied by



ordinary matter, amenable to our senses, as well as to the universal law of gravitation, must be occupied by a strange and anomalous form of matter amenable to neither? Probabilities appear to negative this question. But it will be immediately asked, how can æther be imagined to avoid pervading our atmosphere and all other kinds and forms of matter? Simply by ascribing to it a property of *non-miscibility* with our atmosphere, like oil with water—a quality not entirely adverse to experience, nor repugnant to reason. The question then naturally arises, what becomes of the waves of heat and light when they reach our atmosphere? and is ordinary matter sufficient and effectual for their transmission? This question can be answered only from analogy, which appears to infer an affirmative.

That sound-waves are transmitted by air, and not by interstitial æther, is unquestionable; and if air be capable of transmitting 25,000 vibrations in one second, it would probably be difficult to assign any valid reason why the same medium is incapable of transmitting the far more rapid waves of heat and light; and if capable, then where lies the necessity for assuming the presence of another medium?

Again, the refraction of sound, as demonstrated by the experiments of Hæjch and Sondhaus (563, 564), is in exact accordance with the laws hitherto assigned to the refraction of light and heat. But the phenomena of the refraction of light require a very forced addendum to the interstitial-æther hypothesis, namely, that the elasticity of the æther is *dependent upon that of the medium which it pervades*—an unprecedented influence of one kind of matter on other merely contiguous matter. And it appears that the velocity of sound in solids and liquids is much greater than in air (545); in water it is nearly 5000 feet, and in iron nearly 17,000 feet in one second: is there, then, any known fact whatever that tends to assign a limit to the *possible* velocity of transmission of wave-motion through these and other material media? if not, then the presence of æther, as generally assumed, cannot be deemed *essential* to the transmission of light; and if not essential, why should the old hypothesis be entertained?

“Nec Deus intersit nisi dignus vindice nodus  
Inciderit.”

Moreover Professor Tyndall, to whom the progress of Dynamical Physics is indebted for many laborious and important researches, has observed that in various kinds of wood there is a remarkable harmony between their respective conductivities for sound and heat in three mutually perpendicular directions, namely, longitudinal, transverse-radial, and transverse-tangential (546). Now, although there is certainly no direct analogy between the conduction of heat and the radiation of light, beyond that of their common dynamical origin, a much closer analogy may nevertheless be traced through the phenomena of phosphorescence, fluorescence, and calorescence. Is it, in fact, generally believed that the transmission of heat-motion is effected by interstitial æther, and not by the molecules of the medium itself? If not, why should a hypothetical medium be as-



sumed for light-motion which is not required for that of heat, since the rapidity of the undulations and their velocity of transmission is so much the same in both? while at the same time the converse permeabilities to light and heat of crystals of alum, and those of dark smoky quartz, present striking examples of the existing yet unknown differences of physical constitution which are met with in the various kinds of matter.

It may further be remarked that the dynamical theory of electricity, if tenable, presents additional reasons for denying the necessity of the presence of æther in ordinary matter. For if the molecules of a rod of copper can transmit an electric wave at the rate of at least 250,000 miles in a second, why cannot those of a rod of glass transmit a wave of light at about three-fourths of that velocity?

If, then, these premises be established, it must be granted that the presence of æther is not *essential* to the transmission of any known kind of wave-motion; and if so, is it not more in accordance with the true spirit of philosophy, in default of positive knowledge, to abandon unhesitatingly the more violent hypothesis, and to adopt provisionally the more reasonable one above suggested?

The phenomena of phosphorescence present further evidence of the intimate relations existing between electricity, heat, and light. It has been observed that fluor-spar may be rendered phosphorescent by a very moderate application of heat, but that it will not again phosphoresce under similar circumstances until an electric spark has been repeatedly passed over its surface. Is it not probable that the phosphorescence by heat of the minerals fluor and apatite and ordinary incandescence are similar phenomena, differing only in the temperature (*amount of vis viva*) at which heat-motion impressed on the molecules of different bodies is imparted as light-motion to the surrounding medium.

Our ideas of *vis viva* and its relation to "accumulated work" are inseparably associated with that of gravitation; is it not, therefore, something like a contradiction in terms to speak of the *vis viva* of an *imponderable* body? But if æther be not supposed to be intermingled with palpable matter, then there is no object in attributing to it an exemption from the otherwise universal law of gravitation; and it will then be imperceptible only because it exists beyond our reach. Moreover, as there are no means of limiting the possible amount of molecular displacement in a medium so attenuated, an amount of *vis viva* is conceivable sufficient to impart effective motion to indefinitely denser matter; and thus this denizen of infinity may be assumed capable of executing its divine mission of imparting to material worlds those essentials to corporeal existence, the very main-springs of organic life—light and heat.

If these things are so, then (in American common parlance) "the bottom falls out" of an experiment lately shown at the Royal Institution to demonstrate the presence of æther by the

heat developed in a metallic disk rotating rapidly in the exhausted receiver of an air-pump\*. That the periodic retardation of Encke's comet is due to the resistance of the universal medium is highly probable; but this experiment, if it proves anything in the same direction, proves a great deal too much: for if such be the viscosity of the medium hypothetically present in the receiver, that the addition of a notable quantity of air (5 or 10 per cent. as was stated) makes no sensible difference in the heat generated by friction, it is difficult to conceive how any of us have hitherto escaped resolution into our gaseous elements. On the contrary, when our earth and its envelope enters a probable atmosphere of orbitating fragments (of which we have recently had such a magnificent experience), some of these crumbs of the universe which have for an indefinite period harmlessly traversed the æthereal medium of infinite space, at the enormous velocity of perhaps 30 or 40 miles in a second, become immediately ignited, and probably consumed by friction in the confines of our atmosphere, which must there be attenuated to a degree never yet attained, except perhaps in the vacuum-tubes of Mr. Gassiot.

Permit me in conclusion to repudiate (needlessly perhaps) any claim to originality in the general idea that the molecules of palpable mater are permeable to the undulations of light, which has long since been ably advocated by Euler and by Mr. Grove†.

I remain,

Yours faithfully,

CHARLES BROOKE.

LXXI. *On the Tones produced by Rotating Tuning-forks.*

By Professor W. BEETZ‡.

THE brothers Weber, in their investigations into the laws of waves, have described the following experiment §:—"If a tuning-fork is fixed in a lathe so that it can be made to revolve about the longitudinal axis of the stem, the sound of the vibrating fork is observed to cease when the speed of revolution has reached a certain point, but it becomes again perceptible if the driving-wheel of the lathe is suddenly stopped. This phenomenon cannot be explained by supposing it to be due to the drowning of the sound of the fork by the noise of the lathe; for even when one end of a cylindrical tube is brought near the prongs, and the ear is put at the other end of the tube, it becomes

\* Proceedings of the Royal Institution, vol. iv. p. 563. The writer has since learnt that the æther-friction theory has been judiciously withdrawn by its author for further consideration.

† Correlation of Physical Forces, p. 163, &c.

‡ Communicated by the Author, from Poggendorff's *Annalen*, vol. cxxviii. p. 490 (August 1866).

§ *Wellenlehre*, p. 519.

evident that the rotation does not prevent the vibration of the tuning-fork, but simply the communication of the motion to the air. As yet we are unable to give any explanation of this remarkable phenomenon."

I repeated this experiment a long time ago, but arrived at a quite different result, an account of which I laid before the Physical Society of Berlin\*. I in fact never heard the sound of the tuning-fork cease, but only become weaker; but I distinctly heard at the same time a higher tone, as well as a series of beats which coincided in number with the number of half-revolutions of the tuning-fork. MM. W. and E. H. Weber, to whom I communicated my discordant result, unfortunately could not again find the tuning-fork which they had used. Professor W. Weber, however, wrote me that it was a common *aa*-fork, and suggested that the reason why the higher tone had not been perceptible in their experiments was that they had employed a slower and more noisy lathe. But a satisfactory explanation was still wanting.

My attention was lately recalled to this almost forgotten observation by König's beautiful experiment, in which the tone of a tuning-fork sounds higher when it is approaching the ear, so that the number of beats which it gave with another fork while at rest is altered by its motion†. The idea easily suggested itself that tones of different pitch must reach the ear from the two prongs of the rotating tuning-fork, since one is moving towards the ear and the other away from it. I consequently took up my experiments again; but this time they have led me to an entirely different view of the phenomenon.

The excellent tuning-forks which are now available allow of the experiment being made in a very decisive manner. I used principally a "middle *c*"-fork (512 vibrations), by Lange of Berlin, and a *cc*-fork (1024 vibrations‡), by König of Paris; the prongs of the former were 155 millims. long, and those of the latter 100 millims. The section of the prongs of both forks was rectangular, as is usually the case in tuning-forks; at the point, the prongs of the "middle *c*"-fork measured 11 millims. by 6 millims., and those of the *cc*-fork 14 millims. by 6 millims., the smaller dimension being in both cases in the direction in which the fork vibrates when sounded. When these forks were fixed in the lathe and set in rotation at the rate of about twelve turns in a second, after being caused to vibrate, the tone *c* rose about three-quarters of a tone, and *cc* a little more than half a tone.

\* *Fortschritte der Physik*, 1850-51, vols. viii & ix. p. viii.

† König, *Catalogue des appareils d'Acoustique*, p. 16, No. 75.

‡ [The above numbers correspond respectively to 256 and 512 complete vibrations, according to the mode of counting usually adopted in England.—TRANSL.]



At the same time the beats already mentioned were noticed, two occurring in every revolution. In order to make the rise of pitch distinct to those who have difficulty in discriminating pitch, it is only necessary to place a sounding-box directly under the rotating fork. If the box be tuned to the pitch of the fork, on slowly turning the latter the phenomenon of interference observed by the brothers Weber is perceived. On turning more rapidly, the tone of fork makes a squalling slide upwards; but if the sounding-box is now tuned gradually higher, the tone becomes clearer and clearer until the pitch has been raised to the extent above stated. The rise of pitch is likewise heard exceedingly well when a Helmholtz's resonator, tuned to the note of the rotating fork, is put into the ear. This phenomenon, however, has nothing whatever to do with the communication of sound by the sounding body to the air, or with its propagation by the latter; for the rise of pitch and the beats are heard as well, or even better, when the ears are stopped and the head is rested against any part of the lathe. The phenomenon is thus entirely objective, and consists in a real increase of the rate of vibration of the fork. It is in fact only another form of Foucault's pendulum-experiment. The vibrations tend to continue in the same plane as that in which they were produced; they are thus, as it were, transmitted to a thicker bar, and so produce a higher tone. The amplitude of the vibrations at the same time becomes smaller; gradually, however, it increases again, and reaches a minimum\* every time that the fork returns to its original position, or to one differing from it by  $180^\circ$ . It is thus that the beats are produced; the number of them is consequently of course only half as great as that of the beats heard in Weber's interference-experiment. If the fork turns only slowly, the plane of vibration turns with it, and in this case the fundamental tone is heard alone without beats; on turning more quickly, objective-beats soon arise, and the tone rises at the same time, but never to an extent corresponding to the vibrations of a rod whose thickness is equal to the longer cross section of the prongs of the fork.

In confirmation of the correctness of this explanation, I also made experiments with two smaller forks to which I could give a speed of 25 turns per second upon a rotation-apparatus which ran very noiselessly. The prongs of one of the forks (*gg*) were 6 millims. wide and 1.5 millim. thick (the thickness being measured in the direction in which the bow is applied to the fork to make it sound); the prongs of the other (*cc*) were 1.5 millim. wide and 6 millims. thick. When the forks were set in rotation, the tone of the *gg* fork rose a fourth, and that of the *cc* fork fell half a tone. In the case of the latter fork, a third and

† [Query, a maximum?—TRANSL.]



somewhat higher tone could be heard, due, no doubt, to the greatest thickness of the prongs being in the direction of the diagonal of their cross section, and the plane of vibration having to pass through this direction before it could reach that of their width.

The experiment is much more striking, because simpler, when it is made with a single rod instead of with a tuning-fork. I could not find a rod which would sound loud enough and long enough when fixed at one end; but the experiment succeeds admirably with a rod which is free at both ends. A steel rod 1 metre long, 16 millims. wide, and 8 millims. thick was hung by one end to a thread which formed a prolongation of the axis of the rod. If I now grasped any one of its nodal points gently between my finger and thumb, and caused it to sound by a blow with a soft hammer, I obtained the note corresponding to its width or to its thickness, according to the direction in which I struck it,—for instance, when it was vibrating with five nodal points in the direction of the thickness, the tone *gg*; and when it vibrated similarly in the direction of the width, the tone *g*. If, however, the rod is struck in the former direction and then turned round through  $90^\circ$ , the tone *g* is heard distinctly and almost by itself; while, if it is struck in the latter direction and then turned through  $90^\circ$ , the tone *gg* is heard as distinctly. Here, then, the plane of vibration actually remains quite constant. If the thread is twisted and then let go after the rod has been struck, both notes are produced as the rod rotates, and in the intervals a droning of other tones corresponding to oblique directions across the sectional surfaces. A cylindrical rod treated just in the same way, gave its fundamental note as a continuous steady sound. If the parallelepipedic rod is allowed to hang quietly while sounding, and the ear is carried round it, no changes of tone are perceived; but if it is hung by a twisted thread held between the teeth, the ears being stopped, the alternations of tone and the beats are at once heard. The phenomenon is consequently here again completely independent of the propagation of sound through the air.

I attempted to make the phenomenon visible by means of a Wheatstone's kalcidophone, using for the purpose a beautiful instrument by König, with six rods. The experiment succeeds very well with the cylindrical rod, as has been already described by Foucault\*. The vibration-figure as seen in the knob, whether the straight line, the ellipse, or the circle, remained quite stationary, thus proving that the plane of vibration was really constant. I hoped to see a similar stability in the vibration-curves of the other rods; but with these such entangled forms were produced that I abandoned all the rest and confined myself to

\* *L'Institut*, No. 920, p. 260. *Fortschritte der Physik*, 1850-51, p. 120

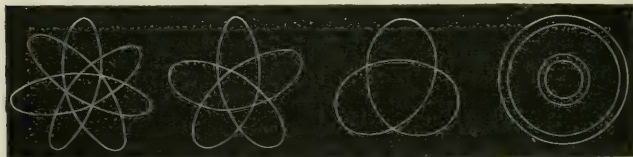
the straight line produced by a blow perpendicular to one of the faces of the rods. On setting the rod in rotation, this straight line by no means remained at rest; on the contrary, figures were produced which I was surprised to find were alike for all the rods, though their width and thickness bore the most varied proportions to each other, but which depended on the rate of rotation. On turning slowly, figures like fig. 1 were produced, which, as the speed was raised, passed into figs. 2, 3, and lastly into fig. 4, the last being composed of two concentric luminous circles upon a less brightly illuminated ground. Intermediate

Fig. 1.

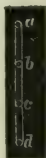
Fig. 2.

Fig. 3.

Fig. 4.



rates of rotation gave figures formed by lines which did not return into themselves, and which therefore had a less sharply marked appearance. All these figures arise in the following manner:—If the plane of vibration of a rod remained constant, its vibrations would have a smaller amplitude in the direction of its greatest thickness, and a larger amplitude in that of its least thickness. Hence we should see a stationary streak of light, in which the turning points *a*, *b*, *c*, and *d* (fig. 5), Fig. 5. where the knob is momentarily at rest, would appear brightest. Such freedom of motion is, however, only partially possible in the case of the firmly fixed prismatic rod; and consequently the figure turns round, more slowly than the rod, but quickly enough to produce the appearance shown in fig. 4. The more slowly the rod rotates, in comparison with its number of vibrations, the oftener does its shifting principal plane of vibration cross its original position of equilibrium during one revolution; and thus are produced knotted or looped figures, among which figs. 3, 2, 1, and others, with still more loops, are the only ones which stand out with special distinctness, in consequence of their being formed by lines returning into themselves. Their form is consequently quite independent of the ratio between the width and thickness of the rods; but figures with many loops are less readily formed in proportion as the rod vibrates more slowly. The figures which a rod which is not vibrating at right angles to one of its faces exhibits on rotation are compounded of these and the well-known kaleidophonic figures.



Erlangen, June 1866.

*Note on the foregoing Paper.* By Professor G. C. FOSTER.

On repeating the remarkable experiment which forms the starting-point of Professor Beetz's interesting paper, I obtained, as was of course to be expected, a result completely in accordance with what he has described. A *gg* tuning-fork, by König, making 384 complete vibrations per second (marked "*Sol*<sub>3</sub> 768"), the prongs of which were 115 millims. long by 15 millims. wide and 7.5 millims. thick, was set in rotation by means of a lathe at the rate of from eighteen to twenty turns per second. Under these circumstances its tone rose almost exactly a *minor third*, the alteration of pitch being judged of by comparison with an organ-pipe whose note could be altered by means of a sliding paper tube put on at the top. The effect upon the ear of the rapid succession of beats which accompanied the tone of the rotating fork was exactly that of a harsh discord, thus affording a striking illustration of Helmholtz's theory of the nature of discords in general (*Tonempfindungen*, pp. 251 *et seq.*, also p. 293).

The principle of Professor Beetz's beautiful explanation of his experiments may be very simply illustrated by means of a pendulum whose time of vibration is unequal in two planes at right angles to each other. A ready and effectual means of constructing such a pendulum was pointed out to me two or three years ago by Professor Sir William Thomson: it consists in fastening the two ends of a piece of string to two points in the same horizontal line, the distance between them being considerably less than the length of the string, and hanging a weight by a second string to the middle point of the first. The strings and weight thus form a pendulum of the shape of the letter Y. The total length of the pendulum employed by me as an illustration of Professor Beetz's experiments was 56 inches, and the length from the middle point of the line joining the two points of suspension (which were  $20\frac{1}{2}$  inches apart) to the bottom of the fork of the Y was 42 inches; so that its time of vibration in the vertical plane containing the points of suspension was half as great as its time of vibration perpendicularly to this plane. On giving the pendulum a small motion in the former plane and then suddenly causing the line joining the points of suspension to turn horizontally about its middle point through  $90^\circ$ , the pendulum still oscillated almost exclusively in its original plane, but its time of oscillation was doubled and the amplitude also increased; on turning the line of suspension through  $90^\circ$  more, or back again to its former position, the pendulum oscillated as at first. In order that this experiment may succeed well, it is needful to alter the position of the line of suspension as rapidly as possible; if it is turned slowly, the plane of oscillation of the pendulum turns with it, and nearly to the same extent.



LXXII. *Limited Oxidation.* By J. ALFRED WANKLYN, *Professor of Chemistry at the London Institution*\*.

IN writing the chemical history of an organic substance, chemists frequently assign an important place to the products of oxidation, which they sometimes make use of to aid in determining the structure of the substance and its place in the general chemical system.

Of late years increasing attention has been paid to these oxidation-products, which, owing to the labours of Kolbe, Berthelot, Wurtz, and the researches which have been carried on in the laboratory of the London Institution, have assumed an unlooked-for importance, and the study of which is so full of the promise of an insight into the mysteries of chemical structure.

Notwithstanding all this, the processes of oxidation hitherto used by chemists are crude and wanting in precision—always excepting the grand fundamental oxidation known as “The Elementary Analysis” or “Combustion,” which is the very type of certainty and precision.

If we refer to Limpricht’s excellent *Lehrbuch der organischen Chemie*, 1862, p. 118, we find that when alcohol is distilled with bichromate of potash and dilute sulphuric acid, or with peroxide of manganese and dilute sulphuric acid, it gives aldehyde, acetic acid, formic acid, acetic ether, and acetal. We read moreover that when the oxidation of alcohol is effected by means of nitric acid in the cold, glyoxal, glyoxylic acid, glycolic acid, oxalic acid, acetic acid, and formic acid figure as oxidation-products. In fact, the prevalent idea of the oxidation-process, as was well expressed by an eminent chemist on a recent occasion at the Chemical Society, is, that by applying the oxidizing agent one obtains certain proximate products which undergo a gradual breaking up as the oxidation proceeds, giving products of less and less complexity, until the final result is carbonic acid and water.

The attitude taken by chemists towards the oxidation-process was illustrated by myself in 1863, when, in the progress of the research on the hexyl group, working in conjunction with Erlenmeyer, the observation was made that beta-hexyl alcohol gave acids of less complexity than caproic acid. Before I could attach much value to the result, I took care to assure myself that there was no caproic acid produced and then destroyed by the further action of the dilute chromic acid. I took the beta-hexyl alcohol, and distilled rapidly with bichromate of potash and dilute sulphuric acid, taking care that the oxidation was incomplete, and that an oil distilled over along with an aqueous layer of liquid. Potash was added to the oil and the aqueous layer. That portion of the oil insoluble in potash was then put back and oxidized afresh, and so the assurance was attained that, if caproic acid were formed and

\* Communicated by the Author.



capable of even momentary resistance to the action of dilute chromic acid, it would have been preserved. It is worthy of remark that so successful was the effort to obtain the most complex fatty acid which could result, that the butyric acid actually obtained appears to be pseudo-butylic acid.

These examples will serve to give an idea of the state of our knowledge of the oxidation-process up to the present day.

Before proceeding to describe the immense improvement which has been made by Chapman and Thorp in the conduct of the oxidation-process, it is only right to call attention to my own oxidation of the propione got from carbonic oxide and sodium-ethyle. Having totally failed to oxidize propione by distilling it in an open retort with bichromate of potash and dilute sulphuric acid, I sealed it up with excess of bichromate of potash and dilute sulphuric acid, and heated for many hours in the water-bath. The propione slowly disappeared, but, in spite of the prolonged action of the dilute chromic acid, no carbonic acid made its appearance; and after the termination of the experiment, propionic as well as acetic acid was found in the tube. This result, by which the extreme persistence of propionic and acetic acids was established, is the germ which, in the hands of my friends Chapman and Thorp, has developed so magnificently. Chapman and Thorp have shown that, although strong chromic acid, as is well known, performs an utter oxidation down to carbonic acid and water, yet dilute chromic acid behaves absolutely differently. The current notion of the oxidation-process is applicable to strong chromic acid, but not to dilute chromic acid. In an aqueous solution of 8 per cent. of bichromate of potash with just enough sulphuric acid to decompose it completely, chemists are furnished with a reagent which is absolutely without action on the acids of the fatty series at temperatures below 100° C. An exception is made for formic acid, which, as has often been remarked, is not a characteristic member of the fatty series.

Not only are the fatty acids unattackable when ready formed, but they are unattackable when *nascent*. And besides the acids of the fatty series, and benzoic acid and perhaps its homologues, organic chemistry hardly includes a compound which is capable of resistance to the prolonged action of this normal solution of chromic acid. It is hardly possible to overrate the importance of this discovery of Chapman and Thorp. Before it all the crudeness and want of precision vanishes from the oxidation-process. We have a second order of combustion—a “limited oxidation”—wherein the place of carbonic acid and water is supplied by the different fatty acids which figure as ultimate products, as unalterable by the oxidation-agent used as are carbonic acid and water by excess of oxygen at a red heat.

LXXIII. *Proceedings of Learned Societies.*

## ROYAL SOCIETY.

[Continued from p. 474.]

November 15, 1866.—Lieutenant-General Sabine, President, in the Chair.

THE following communication was read:—

“Spectroscopic Observations of the Sun.” By J. Norman Lockyer, F.R.A.S.

The two most recent theories dealing with the physical constitution of the sun are due to M. Faye and to Messrs. De la Rue, Balfour Stewart, and Loewy. The chief point of difference in these two theories is the explanation given by each of the phenomena of sun-spots.

Thus, according to M. Faye\*, the interior of the sun is a nebulous gaseous mass of feeble radiating-power, at a temperature of dissociation; the photosphere is, on the other hand, of a high radiating-power, and at a temperature sufficiently low to permit of chemical action. In a sun-spot we see the interior nebulous mass through an opening in the photosphere, caused by an upward current, and the sun-spot is black, by reason of the feeble radiating-power of the nebulous mass.

In the theory held by Messrs. De la Rue, Stewart, and Loewy†, the appearances connected with sun-spots are referred to the effects, cooling and absorptive, of an inrush, or descending current, of the sun’s atmosphere, which is known to be colder than the photosphere.

In June 1865 I communicated to the Royal Astronomical Society‡ some observations (referred to by the authors last named) which had led me independently to the same conclusion as the one announced by them. The observations indicated that, instead of a spot being caused by an *upward* current, it is caused by a *downward* one, and that the results, or, at all events, the concomitants of the downward current are a dimming and possible vaporization of the cloud-masses carried down. I was led to hold that the current had a downward direction by the fact that one of the cloud-masses observed passed in succession, in the space of about two hours, through the various orders of brightness exhibited by *faculae*, general surface, and *penumbrae*.

On March 4th of the present year I commenced a spectroscopic observation of sun-spots, with a view of endeavouring to test the two rival theories, and especially of following up the observations before alluded to.

The method I adopted was to apply a direct-vision spectroscope to my 6½-inch equatoreal (by Messrs. Cooke and Sons) at some distance outside the eyepiece, with its axis coincident with the axis of the telescope prolonged. In front of the slit of the spectroscope was placed

\* Comptes Rendus, vol. lx. pp. 89–138, abstracted in ‘The Reader,’ 4th February, 1865.

† Researches on Solar Physics. Printed for private circulation. Taylor and Francis, 1865.

‡ Monthly Notices Roy. Ast. Soc. vol. xxv. p. 237.

a screen on which the image of the sun was received; in this screen there was also a fine slit corresponding to that of the spectroscope.

By this method it is possible to observe at one time the spectra of the umbra of a spot and of the adjoining photosphere or penumbra; unfortunately, however, favourable conditions of spot (*i. e.* as to size, position on the disk, and absence "of cloudy stratum"), atmosphere, and instrument are rarely coincident. The conditions were by no means all I could have desired when my first observations were made; and, owing to the recent absence of spots, I have had no opportunities of repeating my observations. Hence I should have hesitated still longer to lay them before the Royal Society had not M. Faye again recently called attention to the subject.

On turning the telescope and spectrum-apparatus, driven by clock-work, on to the sun at the date mentioned, in such a manner that the centre of the umbra of the small spot then visible fell on the middle of the slit in the screen, which, like the corresponding one in the spectroscope, was longer than the diameter of the umbra, the solar spectrum was observed in the field of view of the spectroscope with its central portion (corresponding to the diameter of the umbra falling on the slit) greatly enfeebled in brilliancy.

All the absorption-bands, however, visible in the spectrum of the photosphere, above and below, were visible in the spectrum of the spot; they, moreover, appeared thicker where they crossed the spot-spectrum.

I was unable to detect the slightest indication of any bright bands, although the spectrum was sufficiently feeble, I think, to have rendered them unmistakeably visible had there been any.

Should these observations be confirmed by observations of a larger spot free from "cloudy stratum," it will follow, not only that the phenomena presented by a sun-spot are not due to radiation from such a source as that indicated by M. Faye, but that we have in this absorption-hypothesis a complete or partial solution of the problem which has withstood so many attacks.

The dispersive power of the spectroscope employed was not sufficient to enable me to determine whether the decreased brilliancy of the spot-spectrum was due in any measure to a greater number of bands of absorption, nor could I prove whether the thickness of the bands in the spot-spectrum, as compared with their thickness in the photosphere-spectrum, was real or apparent only\*.

On these points, among others, I shall hope, if permitted, to lay the results of future observations before the Royal Society. Seeing that spectrum analysis has already been applied to the stars with such success, it is not too much to think that an attentive and *detailed* spectroscopic examination of the sun's surface may bring us much knowledge bearing on the physical constitution of that luminary. For instance, if the theory of absorption be true, we may suppose that in a deep spot rays might be absorbed which would escape absorption in the higher strata of the atmosphere; hence also the darkness of a line may depend somewhat on the depth of the

\* Irradiation would cause bands of the same thickness to appear thinnest in the more brilliant spectrum.



absorbing atmosphere. May not also some of the variable lines visible in the solar spectrum be due to absorption in the region of spots? and may not the spectroscope afford us evidence of the existence of the “red flames” which total eclipses have revealed to us in the sun’s atmosphere, although they escape all other methods of observation at other times? and if so, may we not learn something from this of the recent outburst of the star in Corona?

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GEOLOGICAL SOCIETY.

[Continued from p. 475.]

November 21, 1866.—Warrington W. Smyth, Esq., M.A., F.R.S.,  
President, in the Chair.

The following communications were read:—

1. “On marine fossiliferous deposits of Secondary Age in New South Wales.” By the Rev. W. B. Clarke, M.A., F.G.S.

In Australia, until the year 1860, the existence of deposits of Secondary age had not been demonstrated, although Sir T. L. Mitchell, in 1846, collected Belemnites and a few other fossils, which are now said to belong to a Lower Secondary formation. Since the year 1860, Secondary fossils have been collected by several explorers; and the author therefore gave a history of their discovery, with lists of the genera and of some of the species found in each locality. His own investigations of the country near the Maranoa River, in Queensland, and the examination of collections sent to him from localities between there and the Flinders River, have led him to the belief there exist in that area formations ranging from the Trias up to the Cretaceous. Mr. Clarke also stated that the deposits occurring on the eastern and western sides of Australia do not seem to be identical, fossils of the age of the Lias and Inferior Oolite having alone been obtained from the latter.

2. “On the Madreporaria of the Infra-lias of South Wales.” By P. Martin Duncan, M.B. Lond., Sec. G.S.

Referring first to Mr. Tawney’s paper on the Sutton Stone, and his own note on the Corals, appended thereto, as having been the firstfruits of the recent researches on the Infra-lias in South Wales, Dr. Duncan stated that in preparing this communication he had been largely indebted to Mr. Charles Moore for the specimens which he had examined, as well as for a considerable amount of information embodied in the descriptions of the deposits. He then described the strata of Brocastle and Ewenny, giving lists of their fossils, and especially of the new species of Madreporaria described in this paper, and illustrated by lithographs prepared for the Palæontographical Society; he then stated his views of their geological position, their relations to, and differences from the zone of *Ammonites Bucklandi* and the strata in France and Luxembourg which have the same homotaxis, and gave a general view of the distribution of the Madreporaria from the Keuper to the zone of *Ammonites Bucklandi*. The chief conclusions were:—(1) that the fossiliferous beds of Sutton, Southerndown, Brocastle, and Ewenny are important members of the series which intervenes between the Trias and the



beds containing *Ammonites Bucklandi*, *Gryphæa incurva*, *Lima gigantea*, &c., and which has been named the Infra-lias; (2) that the Mollusca and certain well-known species of Madreporaria, which are grouped together at Brocastle, have similar relations to each other in the Calcaire de Valogne, in the zone of *Ammonites Moreanus* of the Côte d'Or, and in the Grès de Luxembourg; and (3) that the above-mentioned beds in Wales, constituting a coralliferous horizon, are the equivalents of the Upper beds of the French and Luxembourgian Infra-lias.

3. "On some points in the structure of the *Xiphosura*, having reference to their relationship with the *Eurypterida*." By Henry Woodward, Esq., F.G.S., F.Z.S., of the British Museum.

The author pointed out that Prof. M'Coy's tribe *Pæcilopoda* was intended to include the *Limuli*, with *Eurypterus*, *Pterygotus*, and *Belinurus*. Prof. Huxley had already shown (in 1853) that this classification was founded upon an erroneous interpretation of the fossils, then (1849) only known in England by extremely fragmentary remains.

The object of this communication was to demonstrate that although Prof. M'Coy's classification was based on conjecture rather than upon a minute acquaintance with the anatomy of these extinct forms, yet the subsequent researches of Profs. Agassiz and Hall in America, Prof. Nieszkowski in Russia, and the independent investigations of Mr. J. W. Salter and the author in this country have shown that a close relationship actually does exist between the *Xiphosura* and the *Eurypterida*.

The author then gave a detailed comparison of the structure of these two divisions, which he proposed to call suborders of Dr. Dana's order *Merostomata*. He also pointed out that the *Xiphosura* were divisible into three genera:—1st, *Belinurus*, Baily, having 5 freely articulated thoracic segments, and 3 anchylosed abdominal ones and a telson; 2nd, *Prestwichia*, a new genus, having the thoracic and abdominal segments anchylosed together; and 3rd, *Limulus*, Müller, having a head composed of 7 cephalic and 1 thoracic segments, followed by 5 coalesced thoracic somites bearing branchiæ, and 1 or more coalesced apodal abdominal somites, to which is articulated the telson. Although so great a dissimilarity exists between *Pterygotus* and *Limulus*, yet in the genera *Hemiaspis*, *Exapinurus*, and *Pseudoniscus* we have forms which, in the number of body-rings, are intermediate.

The order *Merostomata* offers a parallel group to the *Decapoda*, the *Eurypterida* representing the *Macrura*, and the *Xiphosura* the *Brachyura*. The author did not, however, intend by this comparison to indicate that *Limulus* was higher in the Crustacean scale than *Pterygotus*, but rather that the former was one of those low but persistent types (like the *Brachiopoda*) which have remained unchanged through long geological ages, whilst forms capable of further development, like *Pterygotus*, have been modified and swept away.

LXXIV. *Intelligence and Miscellaneous Articles.*

THE TANGENT PHOTOMETER. BY DR. FERDINAND BOTHE.

BUNSEN's photometer, and those constructed by Wight and Desaga according to the same principle, depend, as is well known, on the circumstance that a transparent grease-spot on a sheet of paper disappears when both sides of the paper are illuminated with equal brightness. In most cases the flame of the normal candle, serving as unit of light, is directly compared with the light to be measured. In Desaga's instrument, in accordance with the principle of double weighing, it is compared with a gas-flame burning inside a case, which flame is adjusted to the normal candle. In all these instruments a displacement of one or the other of the flames is necessary, which carries with it many inconveniences.

This displacement may be avoided by placing the screen on which is the transparent spot so that it can be turned, and providing it with an alidade, so as to read it off. The brightness of an illuminated surface, independently of the intensity of the source of light and the distance, depends upon the angle at which it is illuminated: it is proportional to the cosine of the angle of incidence, to the sine of the angle which the rays make with the face. If, then, two sources of light to be compared are so placed that their rays cross at right angles, and if the rotating screen be so placed that it is lighted on both sides by these with an equal intensity of light, the angle of irradiation of each must be equal (that is,  $45^\circ$ ) if the spot is to be invisible. With unequal intensity of light, the screen of the bright flame must be turned towards and that of the weaker away from their respective lights to produce disappearance in the spot.

If the angle for the flame of the brightness  $(I) = a$ , it is for the other,  $(I_1) = 90 - a$ , and we have the equations

$$I \sin a = I_1 \sin (90 - a),$$

$$I \tan a = I_1.$$

Hence the intensity of the light of one source as compared with the other may be measured by the tangent of the angle of rotation.

The premisses for the accuracy of this method:—

- (1) Absolute transparency of the greased paper,
- (2) Perfectly scattered reflexion of light—cannot be assumed with complete accuracy. The side directly illuminated always appears brighter than the transparent spot; and hence a double placing of the screen and a twofold reading off are indispensable, the mean value of which gives the true position, and therewith the true value of  $a$ .

The errors arising from the circumstance that the quantity of light not diffused, and also of the light passing through the paper, at different angular positions of the screen must differ are usually outside the limits of observation, and at most only deserve consideration if the angle of inclination of the rays towards the surface is on the one side a very small, and on the other a correspondingly large angle,—a case which cannot occur in the practical use of the instrument.

It must finally be mentioned that, when there is a very great difference of the intensities of light, the angle whose tangent is to

serve as measure may easily be too large, and hence the accuracy of the observation be materially restricted. In such cases it is best to place from the outset the stronger source of light at double or treble the distance, and to multiply the corresponding angles by 4 or by 9. For use in the determination of gas-flames, which have usually from 5 or 6 to 10 or 14 times the intensity of the normal candle, it is advisable, owing to the easiness of the multiplication, to replace the distances 2 and 3 by  $1\sqrt{5}$  and  $1\sqrt{10}$ ,—thus, for instance, with a distance of the normal candle of  $0^m.3$ , to place the light to be measured at the distances

$$0^m.3 \times \sqrt{5} = 0^m.6708,$$

$$\text{and } 0^m.3 \times \sqrt{10} = 0.9486;$$

and then multiply the tangent of the angle read off by  $\frac{1}{2}$  or 10.

The instrument I use, as constructed by the skilful maker, Hugo Schickert, in Dresden, is arranged as follows.

In a cylindrical brass box, 1 decimetre in height and diameter, on a stand, on which it can be adjusted at any height, four tubes 3 centimetres in width are inserted, two of which have conical projecting pieces, and two have weak lenses. In this box is the screen moveable about a vertical axis, and provided at the top with an alidade, which moves over the horizontal divided circle, the null-point of which is exactly over the axis of two tubes opposite one another. The null-point of the alidade is in the plane of the paper screen; the angle of the screen, with the vertical plane through the zero-point of the circle, may be read off to ten minutes by a nonius. The conical tubes, which cross at right angles and lead the incident rays against the paper screen, have an arrangement to introduce diaphragms and ground or coloured glass plates, the use of which is advantageous with very strong light, or with flames of unequal brightness. The interior is completely blackened.

To use the apparatus, the vertical axis is placed just over the apex of a right angle drawn on the table, on the legs of which are the two lights to be compared; the screen is then turned until the transparent spot quite disappears from the eye of the observer, who is looking through one ocular tube. An observation is then made through the other tube exactly in the same manner; the mean of the two gives the value to be placed in the calculation of the tangents.

Blackening the sides of the observing-chamber is superfluous; it is sufficient to place behind the flames dark and non-lustrous screens of such a size that the conical tubes, if continued, would cover them.—Poggendorff's *Annalen*, September 1866.

#### CONDUCTIVITY OF MERCURY FOR HEAT. BY G. GRIPON.

This was determined by the method of Despretz and Peclet. Expressed in Peclet's unit it is  $=1.67$  (lead  $=3.84$ ). Hence the conductivity of mercury for heat is  $=0.407$  that of lead. If the conductivity of silver be made equal 100, that of mercury is  $3.54$ ,—that is, greater than that of marble, and somewhat greater than that of gas-coke. As the conductivity of mercury for electricity is  $=1.80$  (silver  $=100$ ), it is seen that these two numbers do not coincide as is the case with solid metals.—*Comptes Rendus*, July 9, 1866.



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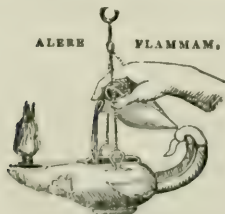
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